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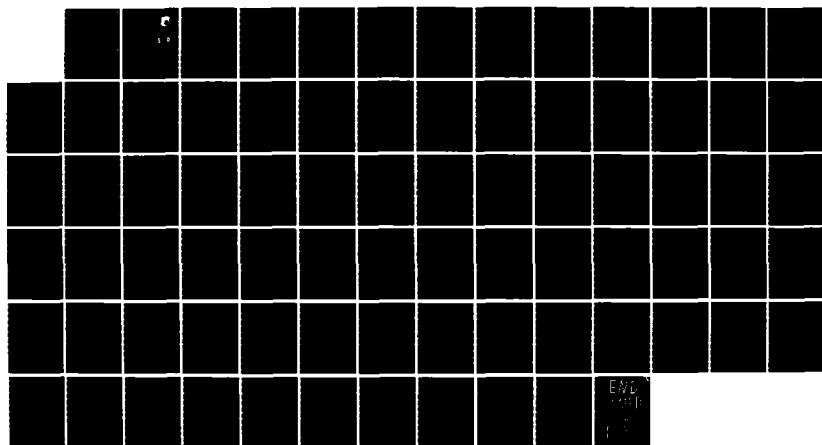
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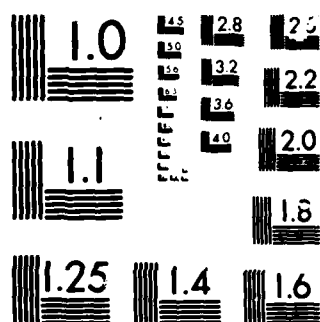
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CHALCOGENIDE GLASSES (PART III)  
CHALCOGENIDE GLASS-FORMING SYSTEMS



AD-A166 592

Koto White  
Laser Hardened Materials Branch  
Electromagnetic Materials Division

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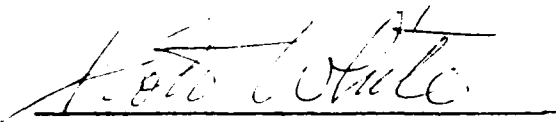
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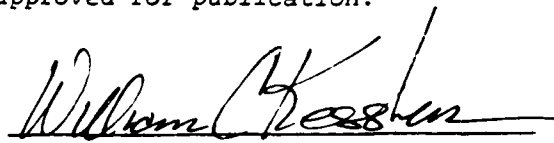
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This technical report has been reviewed and is approved for publication.




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## FOREWORD

This report is a summary of literature search performed at the laser hardened materials branch of the materials laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, from October 1, 1982 to September 30, 1984 under work unit number 24220401. This is the part III of a four part study on chalcogenide glasses.

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## A. INTRODUCTION

Chalcogenide glasses are glasses based on sulfur, selenium and tellurium. Most of the early studies were conducted on the arsenic chalcogenides because of their excellent glass-forming ability. In addition to the arsenic chalcogenides, many chalcogenides containing elements from group IIIA, IVA, VA and VIIA of the periodic table have been discovered to form glasses over wide ranges of compositions, in recent years. Continuous variations of electrical and optical properties, required in some applications, may be achieved by continuously varying the compositions of multicomponent glasses. The usefulness of this approach is severely limited in some multicomponent glasses because of their tendency for phase separation and crystallization, which lead to inhomogeneous microstructures. Because these chalcogen elements form relatively weak bonds with other elements, the chalcogenide glasses in general are softer, electrically more conductive and optically transmitting in further infrared wavelength region as compared to the oxide and fluoride glasses. Among the chalcogenide glasses, the sulfide glasses typically transmit from 0.6 $\mu\text{m}$  to 11.5 $\mu\text{m}$ , the selenium glasses from 1.0 $\mu\text{m}$  to 15.0 $\mu\text{m}$  and telluride glasses from 2.0 $\mu\text{m}$  to 20.0 $\mu\text{m}$ . The oxide and fluoride glasses become opaque around 6 $\mu\text{m}$  and 9 $\mu\text{m}$ , respectively.

Since most compositions are volatile, yet they require relatively high temperatures for complete reaction and homogeneization, the glasses have to be synthesized in either

partially sealed or completely sealed silica tubes. The tube has to be first evacuated prior to complete sealing in order to avoid excessive internal pressure build-up and to minimize oxygen contamination during melting. The glass melts are often kept at temperatures up to  $1100^{\circ}\text{C}$  for as long as several days and agitated for complete homogenization, before quenching to room temperature typically in air or water to form glasses. In a high energy laser application where oxygen, hydrogen and other impurities in the glass cause a problem of high optical absorption at the critical wavelengths, starting materials of 99.9999 percent purity and special glass melting techniques (such as adding aluminum chips as getters to the melt) are required to minimize the impurity.

The compositions with desirable infrared optical properties and generally with high electrical resistance ( $\rho = 10^{13} \sim 10^{18}$  ohm cm) are useful in infrared optics (infrared windows, infrared optical fibers and infrared laser components), while the glasses with semi-conducting properties have applications as switching diodes, electrically activated memory cells, optical storage media and solar cells. Thermally stable chalcogenide glasses have been developed for use in airborne optical systems which must withstand exposure to atmosphere at temperatures above  $500^{\circ}\text{C}$ . The TI-1173 ( $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ ) has been incorporated into the design of of a FLIR (Forward Looking Infrared) system, and TI-20 ( $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ ) has found limited applications as an external window and in prototype optics. Low softening temperature glasses, such as As-Tl-S glass, have been developed for use in

hermetic sealing of electronic components. The selenium glasses have been utilized in the photocopying industry.

This report summarizes the literature search on glass-forming regions of chalcogenide compositional systems. Brief discussions on physical, chemical and structural properties are also included, whenever they are applicable. This study was conducted to select and evaluate the chalcogenide glasses which are suitable for use in graded optical filter applications.

## B. COMPOSITIONAL SYSTEM

### I. One Component Systems

#### 1. Sulfur

The melting point of sulfur varies from 113°C to 115°C, depending on the proportion of orthorhombic form (stable below 95.5°C) and monoclinic form (stable above 95.5°C) present at melting [Ref.1].

The viscosity of sulfur melt does not decrease monotonically with increasing temperature as in other glassy materials. Instead, its viscosity increases rapidly up to around 160°C and reaches its peak at 180°C. This large increase in viscosity is attributed to the breaking of S<sub>8</sub> ring molecules and the formation of long (10<sup>5</sup>~10<sup>6</sup> atoms) sulfur chains. A decrease in the sulfur chain length causes the viscosity to drop at temperatures above 180°C [Ref.2 and 3].

A glassy sulfur can be formed by rapidly quenching the melt from above 160°C to below its glass transition temperature (T<sub>g</sub>=-27°C). Quenching a sulfur melt to room temperature yields a plastic sulfur (amorphous), which quickly crystallizes into orthorhombic form [Ref.4 and 5].

An addition of chlorine, bromine, or iodine to the sulfur melt reduces its viscosity because these halogen elements act as sulfur chain breakers [Ref.6]. This reduction in viscosity enables the atoms to rearrange themselves to a more stable lower energy state during the cooling process. This correlates well

with the fact that there are no glass formations in sulfur halogen systems.

## 2. Selenium

The melting point of selenium is  $217^{\circ}\text{C}$ . Only the hexagonal grey metallic form, consisting of long spiral selenium chains, is thermodynamically stable among five known modifications [Ref.7 and 8]. Since these selenium chains are much shorter than the sulfur chains, selenium has lower viscosity as compared to sulfur at any given temperature. However, the viscosity of selenium just above the melting point is much higher (30 poise) as compared to the viscosity of sulfur immediately above the melting point (0.1 poise) [Ref.1].

A selenium melt easily forms a glass on cooling to room temperature. The glass transition temperature is  $31^{\circ}\text{C}$ . Even though the selenium has a higher melting temperature and a higher glass transition temperature as compared to sulfur, Se-Se bond strength is reported to be lower than S-S bonding strength [Ref.1].

The halogens, alkali metals, thallium, and tellurium reduce the viscosity of selenium by terminating chains or by weakening bonds, and accelerate crystallization.

## 3. Tellurium

The melting point of tellurium is  $453^{\circ}\text{C}$ . The viscosity of a tellurium melt just above its melting point is relatively high ( $\sim 1$  poise), indicating the presence of tellurium chains.

However, it rapidly approaches the viscosity of molten metal ( $\sim 0.001$  poise) on further heating, indicating the collapse of the tellurium chain structure [Ref.1].

Only the hexagonal crystal form has been reported and stable tellurium glass has not been found. A metastable tellurium glass has been synthesized by condensing tellurium vapor onto a liquid air cooled surface. However, the glass rapidly crystallized at  $25^{\circ}\text{C}$ - $30^{\circ}\text{C}$  [Ref.9].



## II. Binary Chalcogenide Glasses

### 1. S-Se

Selenium forms copolymers with sulfur, however, the concentration of monomer increases with increasing sulfur content [Ref.10].

The glass-forming region in sulfur-selenium binary systems extends from 60 to 100 weight percent selenium content, under slow cooling conditions. The glasses in this compositional region, especially the sulfur rich glasses, tend to crystallize at elevated temperatures [Ref.11, 12 and 13].

### 2. Se-Te

An addition of tellurium to the selenium glass enhances crystallization of selenium. This is caused by a reduced viscosity, which in turn is probably caused from a weaker Se-Te bond in the chain structure [Ref.1].

The electrical conductivity of the binary glass has been found to increase with increasing tellurium concentration, indicating that the composition became more metallic [Ref.14].

### 3. As-S

Arsenic trisulfide ( $\text{As}_2\text{S}_3$ ) glass has been used for some time for bulk infrared optics and for coatings because of its excellent far infrared transmission, its persistent glass-forming tendency and its resistance to moisture and chemicals.

Frerichs synthesized optical grade As-S glasses by

distillation in a flowing  $H_2S$  atmosphere, followed by subsequent annealing and slow cooling [Ref.15]. The glasses with between 20 and 60 weight percent sulfur content showed no sign of devitrification after several months at room temperature. However, the glass containing 80 weight percent sulfur was flexible and crystallized within a few days. These glasses exhibited optical absorption bands at  $7.8\mu m$ ,  $10.8\mu m$  and  $11.9\mu m$  (characteristic of plastic sulfur) with increasing sulfur contents. Flaschen et al [Ref.11] reported that the slow cooled As-S glasses exhibited glass formation from 30 to 90 weight percent sulfur ( $As_{44}S_{56}$ - $As_5S_{95}$ ). This glass-forming region agrees better with values indicated in other literature [Ref.16 and 17]. The glasses with sulfur concentrations lower than 30 weight percent are reported to crystallize upon heating, exhibiting crystalline AsS diffraction lines in X-ray analysis. Glass-glass phase separation has been observed for composition range  $As_2S_{2.5}$ - $As_2S_{2.67}$  [Ref.18].

The glass transition temperature ( $T_g$ ) varies from  $30^\circ C$  to  $200^\circ C$  in the glass-forming compositional range, and  $T_g$  has the maximum value at  $As_2S_3$  (Figure 1) [Ref.17 and 19]. Vinogradova [Ref.16] detected maximum at  $As_2S_5$ , as well as the maximum at  $As_2S_3$ , in  $T_g$  and microhardness measurement, indicating a possible compound formation or an existence of a more rigid structure at  $As_2S_5$ . Most of the As-S melts are still highly viscous at temperatures in excess of  $400^\circ C$ .  $As_2S_3$  glass is a high resistivity semi-conductor with the room temperature conductivity of  $10^{-18} ohm^{-1} cm^{-1}$  [Ref.20].

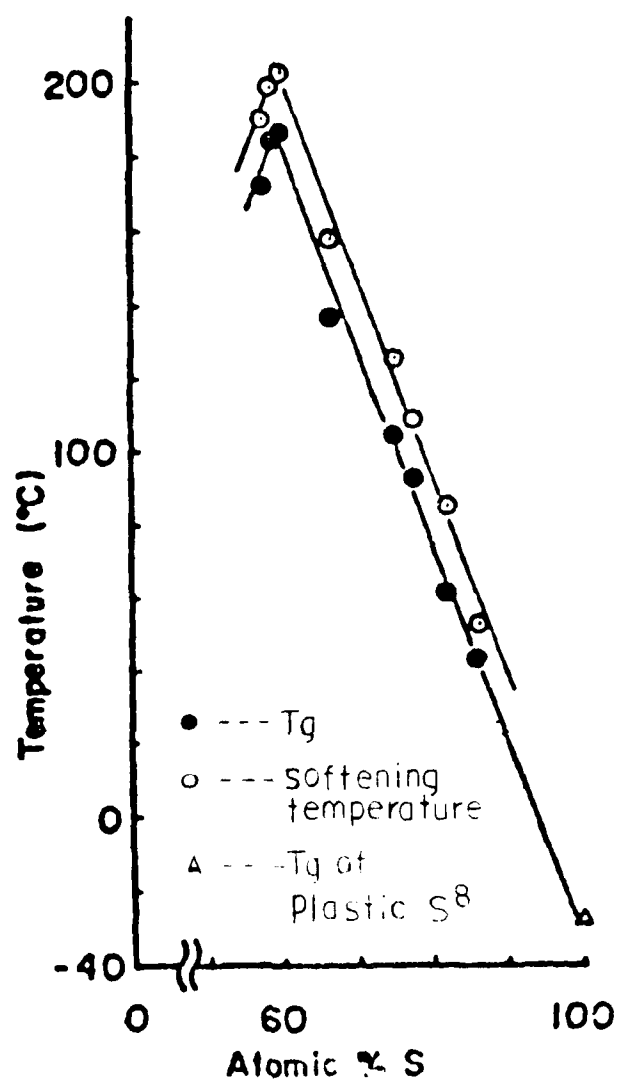


Figure 1. Glass Transition Temperature and Softening Temperature of As-S System [Ref.17]

#### 4. As-Se

Arsenic triselenide ( $\text{As}_2\text{Se}_3$ ) glass is the most studied chalcogenide glass to date because of its importance in optical applications. Its glass-forming tendency is even stronger and its optical transmission extends to further infrared as compared to arsenic trisulfide glass [Ref.10].

Flaschen et al [Ref.11] determined the glass-forming region in As-Se binary system to be between 40 and 100 weight percent selenium ( $\text{As}_{61}\text{Se}_{39}$ -Se ).

$T_g$  varies from  $30^\circ\text{C}$  to  $150^\circ\text{C}$  in slightly non-linear fashion as shown in Figure 2, and has a maximum at the stoichiometric composition  $\text{As}_2\text{Se}_3$  [Ref.21]. Myers et al reported a stronger non-linearity in compositional dependence of  $T_g$  [Ref.19], which suggests the existence of immiscibility gap extending between 70 and 90 atomic percent selenium concentration. Data on viscosity and crystallization kinetics are reported in Ref.22, 23 and 24.

#### 5. As-Te

Glassy arsenic tritelluride ( $\text{As}_2\text{Te}_3$ ) can be obtained only by an extreme quenching condition such as vapor condensation [Ref.1 and 10]. However, Tsugane et al [Ref.25] have found glass-forming regions on each side of  $\text{As}_2\text{Te}_3$ , by air quenching small amounts of materials. Tellurium rich region ( $\text{AsTe}_2$ - $\text{AsTe}_4$ ) and arsenic rich region ( $\text{As}_2\text{Te}$ - $\text{As}_4\text{Te}$ ) yielded crystalline/glass two-phase mixtures. Among the compositions studied, only  $\text{AsTe}$  and  $\text{As}_3\text{Te}_2$  were completely glassy. Borisova [Ref.20] also

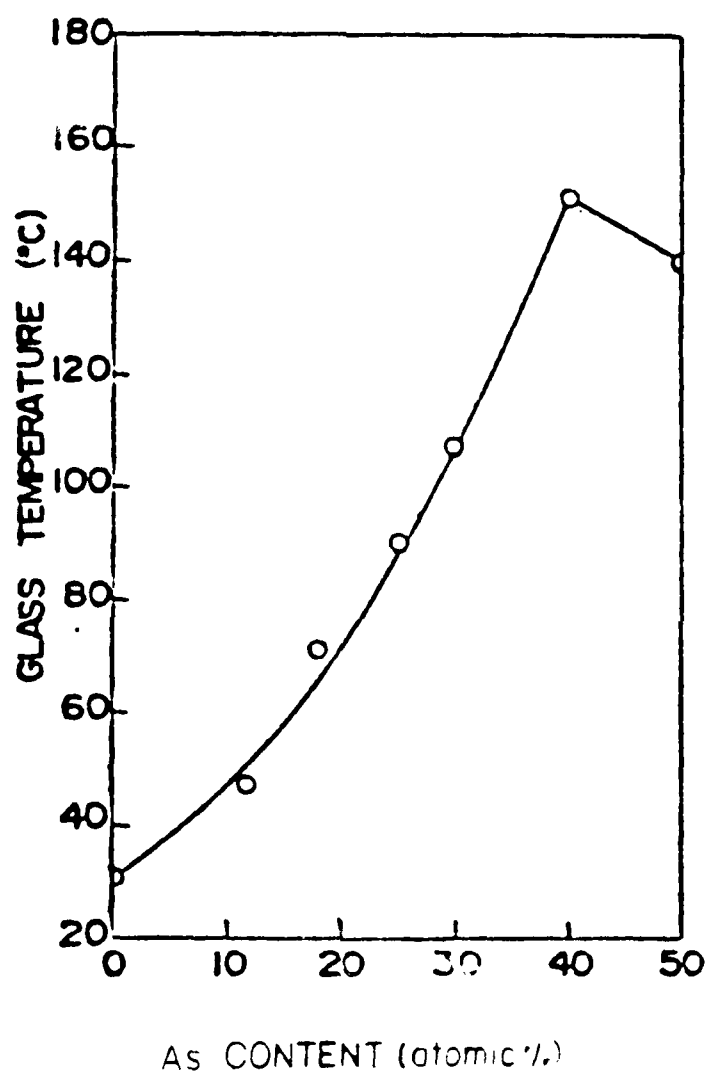


Figure 2. Glass Transition Temperature of As-Se System  
[Ref.21]

produced glassy AsTe and AsTe<sub>0.8</sub> by air quenching.

Cornet and Rossier [Ref.26] examined the crystallization characteristics of these two glass-forming regions using a differential thermal analysis technique.

Hulls et al [Ref.14] observed that a slight oxygen contamination of As-Te melt restricted the glass-forming ability, suggesting an alteration of the glass structure by oxygen. Electrical conductivity was found to increase with increasing tellurium content.

## 6. Ge-S

Germanium disulfide (GeS<sub>2</sub>), along with the As<sub>2</sub>S<sub>3</sub> glass, forms basis for many multicomposition chalcogenide glass systems. GeS<sub>2</sub> glass, which is transparent amber color, is one of a few chalcogenide glasses transmitting in the visible spectral range [Ref.27 and 28].

There is a discrepancy among researchers on the glass forming range in the Ge-S system [Ref.29-35]. Myuller et al [Ref.29] could not produce glasses, either by air quenching or by water quenching the small quantities of the binary compositions which had been reacted at 750°C for 5-6 hours and at 800°C-850°C for 1-2 hours. On the other hand, Hilton et al [Ref.30] have reported a continuous glass formation ranging from Ge<sub>45</sub>S<sub>55</sub> to 100 percent sulfur. They reacted and mixed the binary compositions at 1000°C for at least 16 hours prior to air quenching. Kawamoto and Tsuchihashi [Ref.31 and 32] reported two distinct glass-forming regions; one extends from GeS<sub>0</sub> to GeS<sub>2</sub>

(region I) and another from  $\text{GeS}_{1.5}$  to  $\text{GeS}_{1.3}$  (region II), concluding that the structures of glasses in the two regions are different. In region I, the structure is based on sulfur chains cross linked with germanium, and in region II, it involves  $\text{GeS}_4$  tetrahedral network formers as in  $\text{GeS}_2$  [Ref.33 and 34] and  $\text{GeS}_6$  octahedral network modifiers as in  $\text{GeS}$ . When the sulfur content is greater than that in  $\text{GeS}_4$ , structural microheterogeneity due to miscibility gap may exist.

Glass transition temperature as a function of composition is shown in Figure 3 [Ref.36 and 37].

#### 7. Ge-Se

There is a good agreement among researchers on the glass formation data for Ge-Se binary system. The glass-forming region starts at 70-75 atomic percent selenium and extends up to 100 percent selenium [Ref.35, 38, 39 and 40], for air quenched or furnace cooled specimens. Higher proportion of germanium may be incorporated when the specimen is quenched in liquid nitrogen [Ref.41], or vapor deposited by flash evaporation [Ref.42]. Viscosity and Tg increase with germanium addition. Tg as a function of composition is shown in Figure 4 [Ref.36, 37 and 39].

#### 8. Ge-Te

The telluride glasses are more difficult to form as compared to the corresponding sulfide and selenide glasses [Ref.10]. Pazin et al [Ref.43] reported the glass-forming region in Ge-Te system to be a narrow region between  $\text{Ge}_{15}\text{Te}_{85}$  and near eutectic

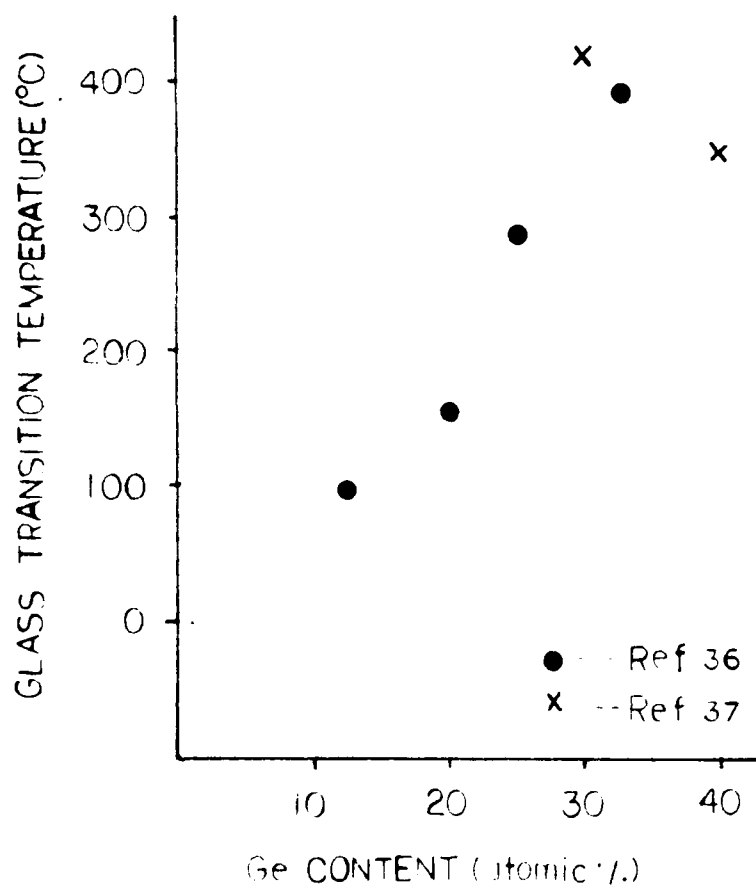


Figure 3. Glass Transition Temperature of Ge-S System  
[plotted from data in Ref.36 and 37]



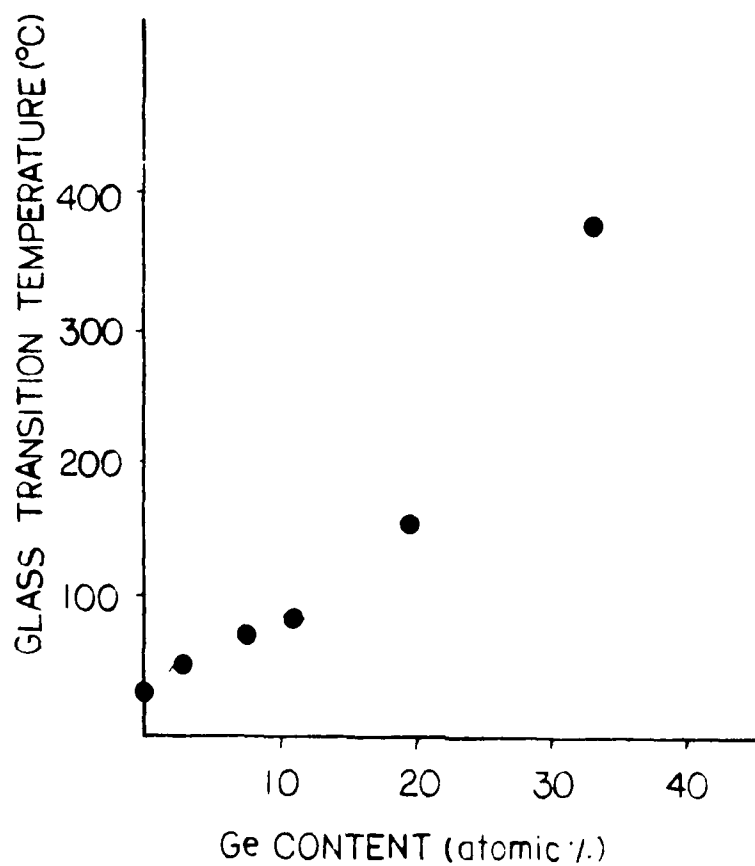


Figure 4. Glass Transition Temperature of Ge-Se System  
[plotted from data in Ref.36]

GeTe under air quench condition.  $T_g$  is  $133^{\circ}\text{C}$  at  $\text{GeTe}_4$  [Ref.44].

#### 9. Si-S

Among silicon-chalcogen binary compositions, glasses have been formed only in Si-S system. Silverman and Soulen [Ref.45] synthesized composition between SiS and  $\text{SiS}_{2.2}$  under high pressure (45 Kbars) in order to overcome the difficulty in glass formation due to the very short liquid range (melting point= $1090^{\circ}\text{C}$  and boiling point= $1130^{\circ}\text{C}$  at normal atmospheric pressure).

#### 10. P-(S or Se)

There is a general tendency of increasing glass stability with decreasing atomic number of the constituent elements. However, the phosphorus chalcogenide glasses do not fit into this general rule. Glass-like materials can be produced in the P-S system at least up to 10 atomic percent phosphorus content, with phosphorus atoms forming crosslinks between the sulfur chains [Ref.1]. Hilton et al [Ref.30] reported much higher limit of phosphorus content (25 atomic percent).

The P-Se system has more extensive glass-forming region, extending from  $\text{P}_{42}\text{Se}_{58}$  to Se [Ref.20]. Goriunova et al [Ref.46] have indicated that stable  $\text{P}_2\text{Se}_3$  glass can be made under slow cooling or quenching condition. The P-Se system is fairly dielectric and the electrical conductivity varies from  $10^{-15} \text{ohm}^{-1} \text{cm}^{-1}$  for a low phosphorus composition to  $10^{-18} \text{ohm}^{-1} \text{cm}^{-1}$  for a high phosphorus selenide.

### III. Ternary Chalcogenide Glasses

#### 1. Ge-Se-Te

Two glass-forming regions, the first one in selenium rich region and the second in germanium rich region, separated by the  $\text{GeSe}_2$ -Te tie line as shown in Figure 5, are reported in Ge-Se-Te system under air quenching condition [Ref.20 and 43]. The glass formation is promoted by elemental selenium and germanium selenides in the first glass-forming region. In the second glass-forming region, vitrification is promoted by formation of more than three types of structural unit with different compositions in the melt.

The density of glasses increases linearly with tellurium content and is virtually independent of the germanium to selenium ratio.  $T_g$  varies from  $89^\circ\text{C}$  to  $336^\circ\text{C}$ , increasing with the germanium content.  $T_g$  is independent of selenium to tellurium ratio in the first glass-forming region, and decreases with increasing tellurium content in the second region. The room temperature electrical conductivity varies from  $10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  at high tellurium content to  $10^{-15} \text{ ohm}^{-1} \text{ cm}^{-1}$  at low tellurium content.

#### 2. P-Se-Te

Figure 6 shows the glass-forming region of P-Se-Te system [Ref.20]. An addition of tellurium into the dielectric P-Se system increases the conductivity by up to 10 orders of magnitude.

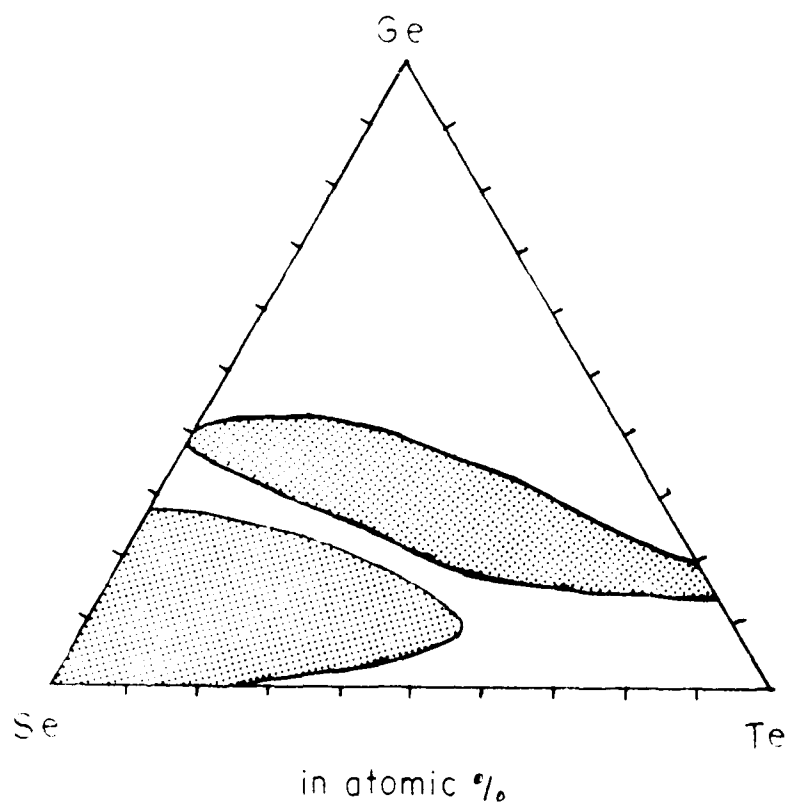


Figure 5. Glass Forming Region in Ge-Se-Te System [Ref.43]

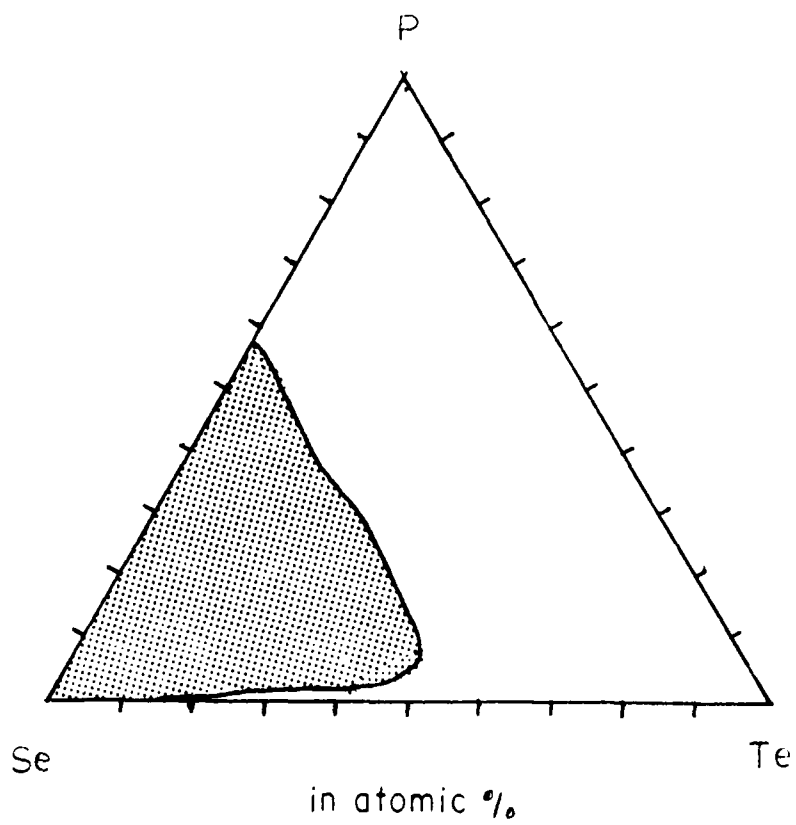


Figure 6. Glass Forming Region in P-Se-Te System [Ref.20]

### 3. As-S-Se

The S-Se glasses are known to devitrify especially at elevated temperatures. An addition of even small amounts of arsenic, however, greatly decreases this devitrifying tendency. The glass formation in the As-S-Se system, even under slow cooling condition, is extensive [Ref.11, 12, 46 and 47]. Figure 7 shows the glass-forming region reported by Flaschen, et al [Ref.11], in which 60 weight percent arsenic can be added without causing crystallization. The temperatures at 30 poise viscosity are also shown in Figure 7, and they vary from 300°C with low arsenic content to 400°C with high arsenic content. Introducing selenium into arsenic sulfides leads to an increase in room temperature conductivity ( $10^{-18} \text{ ohm}^{-1} \text{ cm}^{-1}$  of  $\text{As}_2\text{S}_3$  to  $10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$  at high selenium content), thermal stability and homogeneity. However, this change of properties is relatively insignificant and the properties of the ternary system are basically determined by the structural features of sulfur, even for selenium rich compositions [Ref.20].

As-S-Se glasses may be used as sealing glass because they are chemically durable, have low moisture permeability at room temperature and they bond the metals, ceramics, plastics and silicate glasses [Ref.11 and 12].

### 4. As-S-Te and As-Se-Te

Two separate glass-forming regions are reported for As-S-Te system as shown in Figure 8. The electrical conductivity increases with an addition of tellurium to the As-S binary system

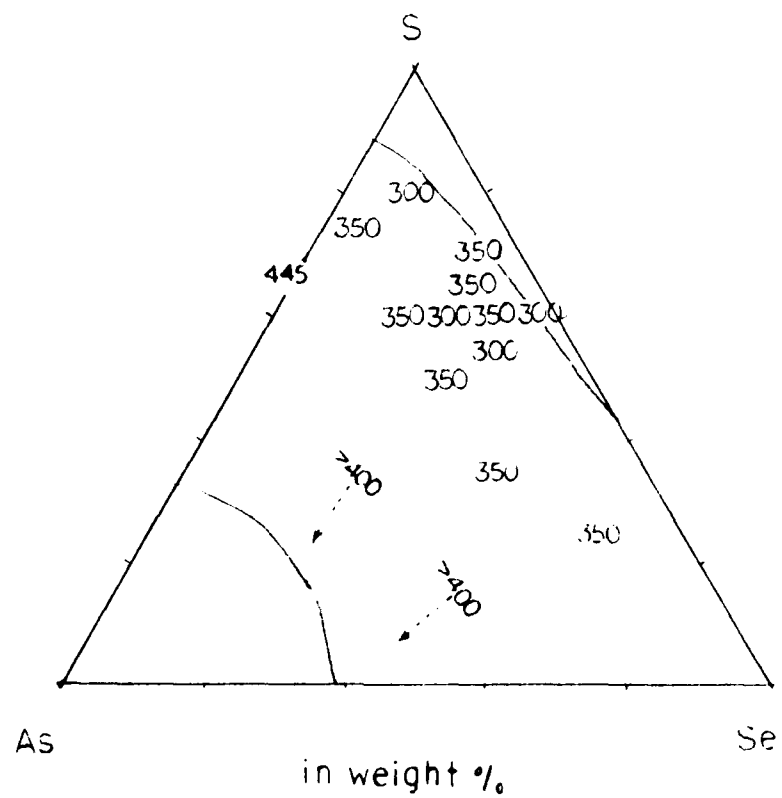


Figure 7. Glass Forming Region in As-S-Se System [Ref.11]

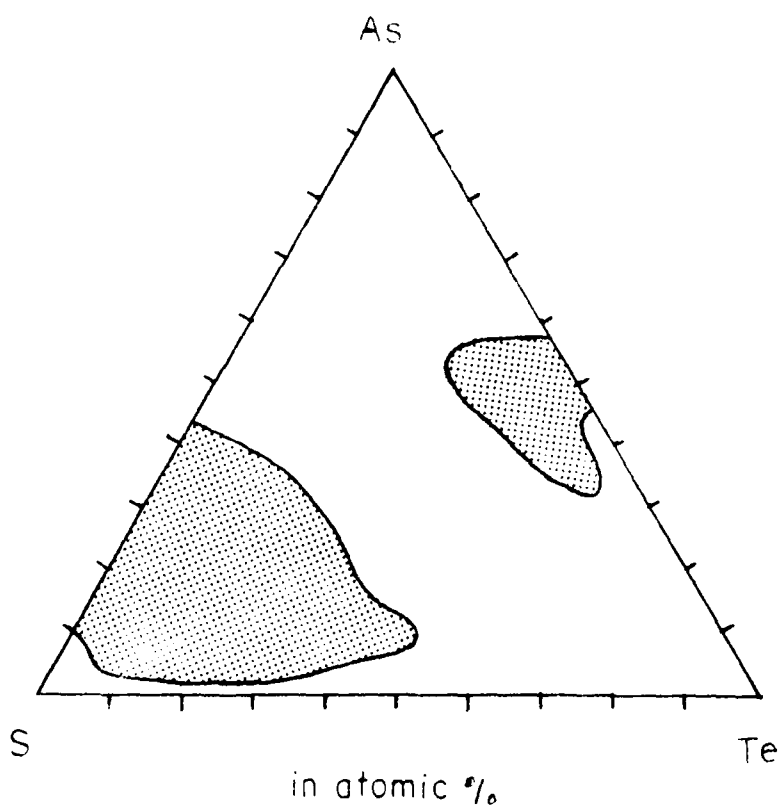


Figure 8. Glass Forming Region in As-S-Te System [Ref.20]



[Ref.20]. Tg increases with increasing arsenic content [Ref.21].

As-Se-Te system has a large glass-forming region [Ref.20 and 46] in selenium rich area as illustrated in Figure 9, under air or water quenching condition. Kinser, et al [Ref.48] reported a bulk threshold memory switching in  $\text{As}_2\text{Te}_3$ - $\text{As}_2\text{Se}_3$  glasses. They correlated this switching phenomena with a liquid-liquid phase separation observed in the microstructure. The more heterogeneous microstructures occurred in  $\text{As}_2\text{Se}_3$  rich glasses, in which better switching stability and higher threshold voltage were observed. The room temperature electrical conductivity varies from  $10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$  for  $\text{As}_2\text{Se}_3$  to  $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$  for  $\text{As}_2\text{Te}_3$  [Ref.14 and 48]. Tg increases with increasing arsenic content [Ref.21].

#### 5. Group IV-P-(S, Se, or Te)

Hilton et al [Ref.30] have reported the glass formations in Si-P-Te (Figure 10), Ge-P-S (Figure 11), and Ge-P-Se (Figure 12). The compositions were reacted and homogenized while in molten state ( $1000^\circ\text{C}$ ) for at least 16 hours. The glasses were formed by subsequent air quenching. The maximum softening points are  $180^\circ\text{C}$ ,  $520^\circ\text{C}$ , and  $420^\circ\text{C}$ , and the refractive indices are 3.4, 2.0-2.3, and 2.4-2.6 for Si-P-Te, Ge-P-S, and Ge-P-Se systems, respectively.

#### 6. Si-As-Te

The glass-forming region of Si-As-Te system is shown in Figure 13 [Ref.49 and 50]. Glasses in this system are

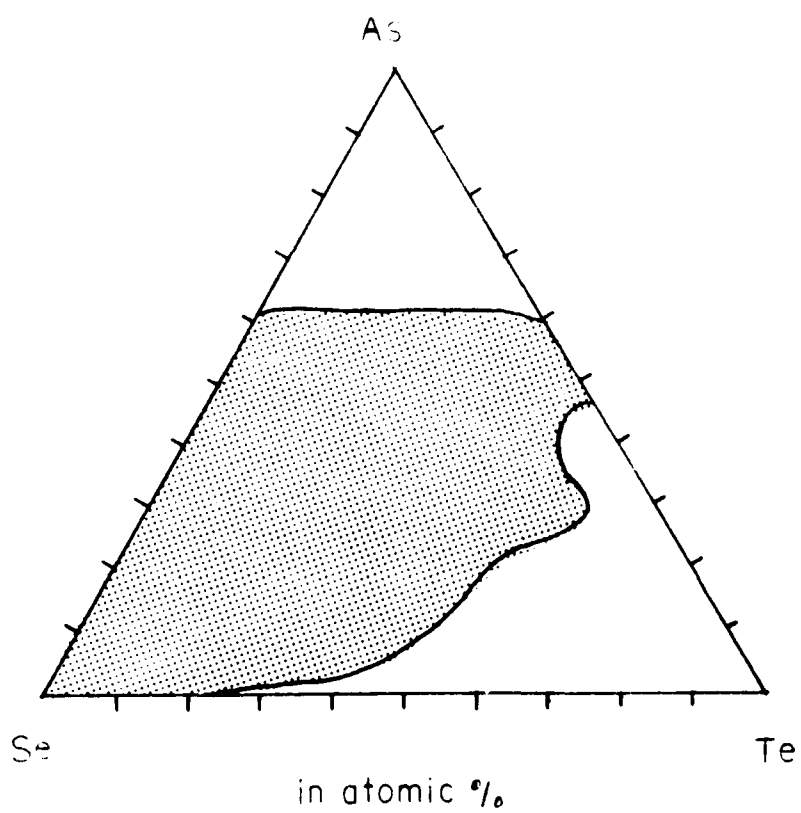


Figure 9. Glass Forming Region in As-Se-Te System [Ref.20]

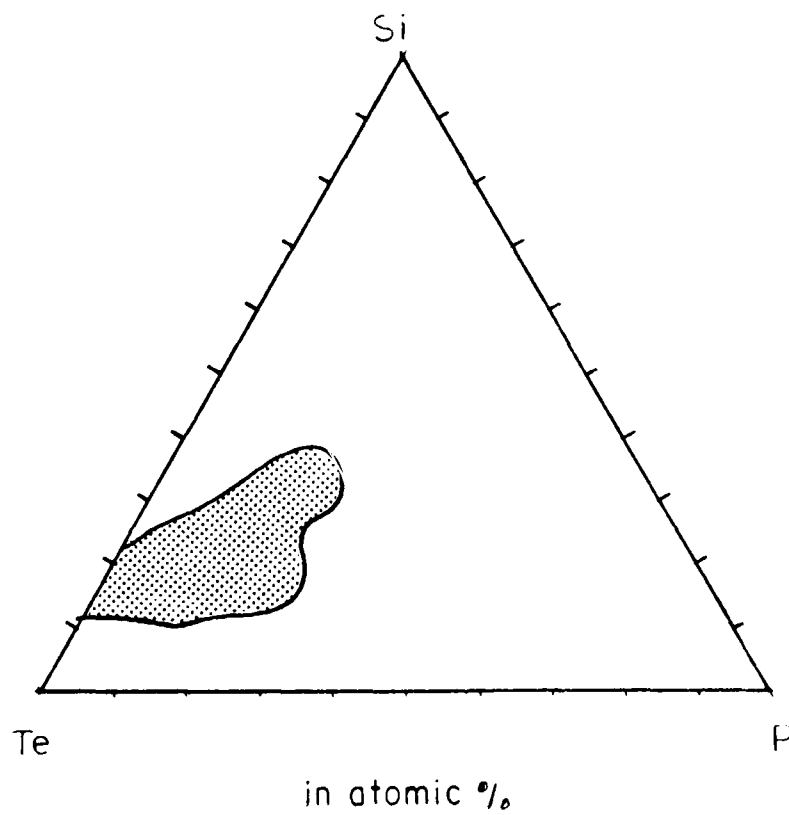


Figure 10. Glass Forming Region in Si-P-Te System [Ref.30]

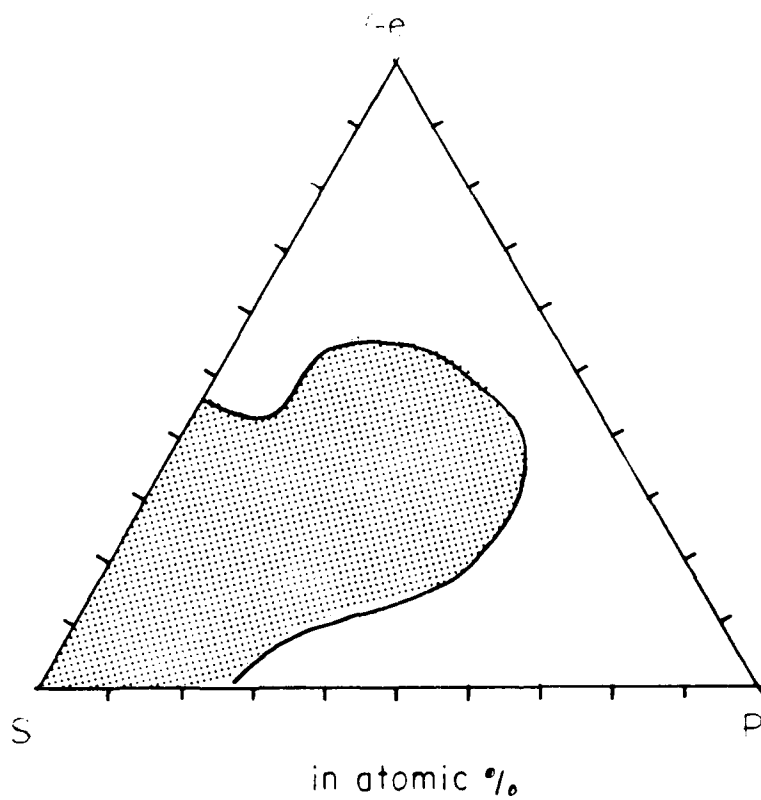


Figure 11. Glass Forming Region in Ge-P-S System [Ref.30]

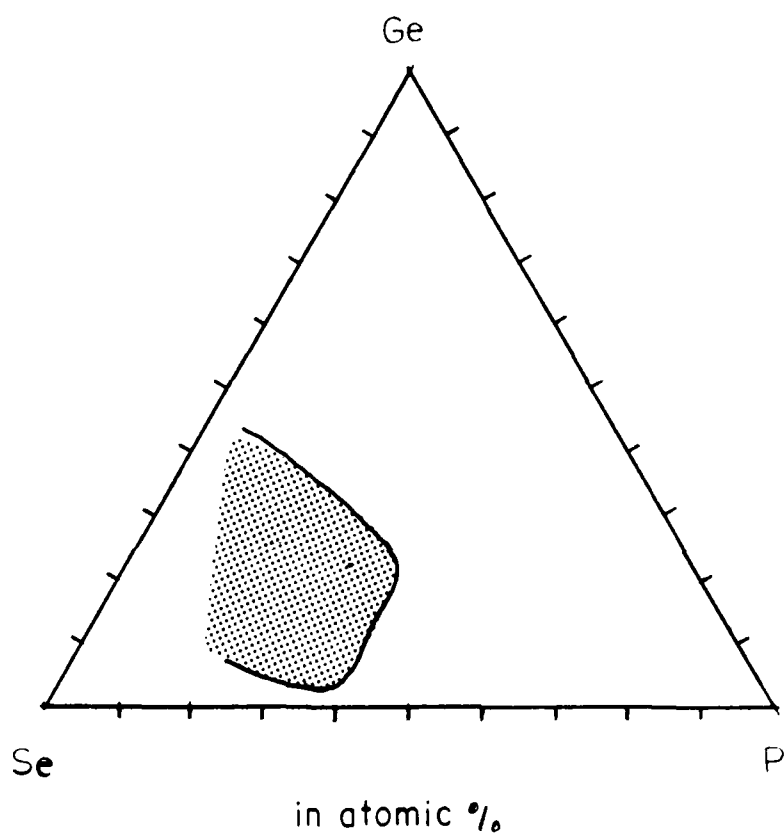


Figure 12. Glass Forming Region in Ge-P-Se System [Ref.30]

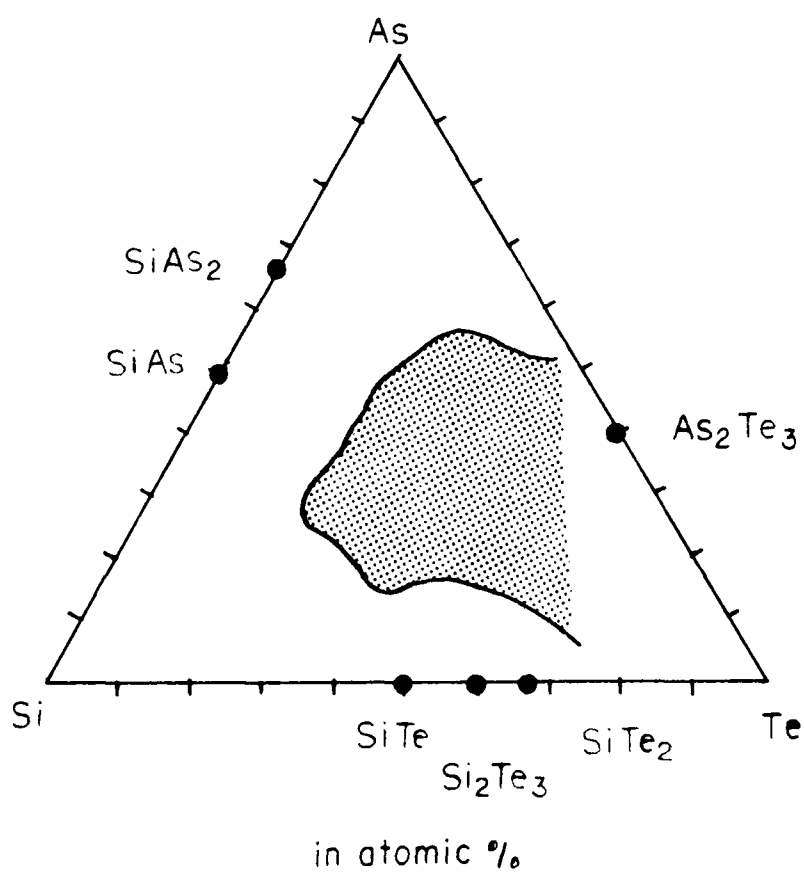


Figure 13. Glass Forming Region in Si-As-Te System [Ref.50]

chemically and thermally stable and have good infrared transmission from  $1\mu\text{m}$  to  $20\mu\text{m}$  wavelength with slight absorption bands at  $10\mu\text{m}$  and  $14\mu\text{m}$  and a strong absorption at  $20\mu\text{m}$ . The softening point is as high as  $500^{\circ}\text{C}$  for a high silicon glass. In practice, Ge-As-Se glasses have been preferred over Si-As-Te glasses because incorporation of silicon in the glass tends to introduce Si-O optical absorption band. Replacing tellurium with selenium in Si-As-Te glasses results in chemically unstable glasses, because silicon promotes decomposition of selenide especially in moist air [Ref.50].

#### 7. Ge-As-S and Ge-As-Se

The glass-forming region in Ge-As-S system is shown in Figure 14 [Ref.29], where the solid line represents the glass formation under air quenching condition and the broken line represents the slow cooling condition. A study on the compositions along the  $\text{As}_2\text{S}_3$ -Ge tie line [Ref.51] revealed that their color changed from dark red to a reddish orange and then back through dark red to near black with increasing germanium content, with the exception of the 5-10 atomic percent germanium range which were a cloudy orange color. X-ray diffraction pattern on these cloudy color specimens showed a small amount of crystalline  $\text{As}_2\text{S}_2$  embedded in a glassy matrix. The density and microhardness generally increased with germanium content with abnormal decrease in the crystallite-forming region.

Hilton et al [Ref.40 and 52] stated that Ge-As-S glasses were superior to Ge-As-Se glasses for infrared optical

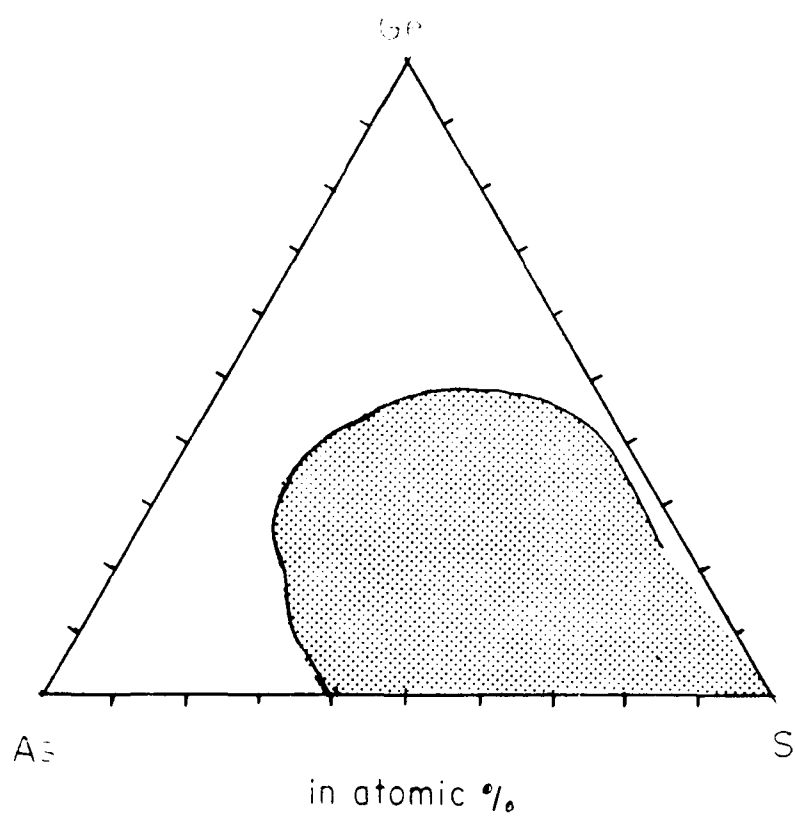


Figure 14. Glass Forming Region in Ge-As-S System [Ref.29]



applications, as far as their physical properties are concerned because the sulfur based glasses had a greater hardness, higher thermal conductivity, higher glass transition temperature and smaller volume expansion coefficient.

The glass-forming region along with the  $T_g$  isotherms in Ge-As-Se system is shown in Figure 15 [Ref.53]. The glass transition temperature varies from 100°C for selenium rich compositions to 400°C for low selenium compositions. Vinogradova et al [Ref.54] reported that annealing at 200°C-500°C for 6 hours -7 days were necessary to crystallize the glass compositions within the glass-forming region.

Glasses in this system are suitable for use as infrared optical components, because they have an excellent optical transmission in 8µm-13µm wavelength region, good thermal stability, low thermal expansion and relatively high  $T_g$ .

The TI-20 glass ( $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ ) is one of a few commercially available infrared optical glasses. However, TI-20 presents problems for application in  $\text{CO}_2$  laser optical systems because its impurity absorption bands at 9.6µm (Si-O), 11.6µm (Ge-O) and 13.0µm (broad band absorption of unknown origin) affect the absorption at 10.6µm  $\text{CO}_2$  wavelength [Ref.39, 49 and 55].

#### 8. Tl-As-S

Region of glass formation for Tl-As-S system [Ref.11 and 46] is shown in Figures 16(a) and 16(b). The temperatures at which Tl-As-S attain a viscosity of 30 poise are included in Figure 16(a), and the softening temperatures are shown in Figure 16(b).

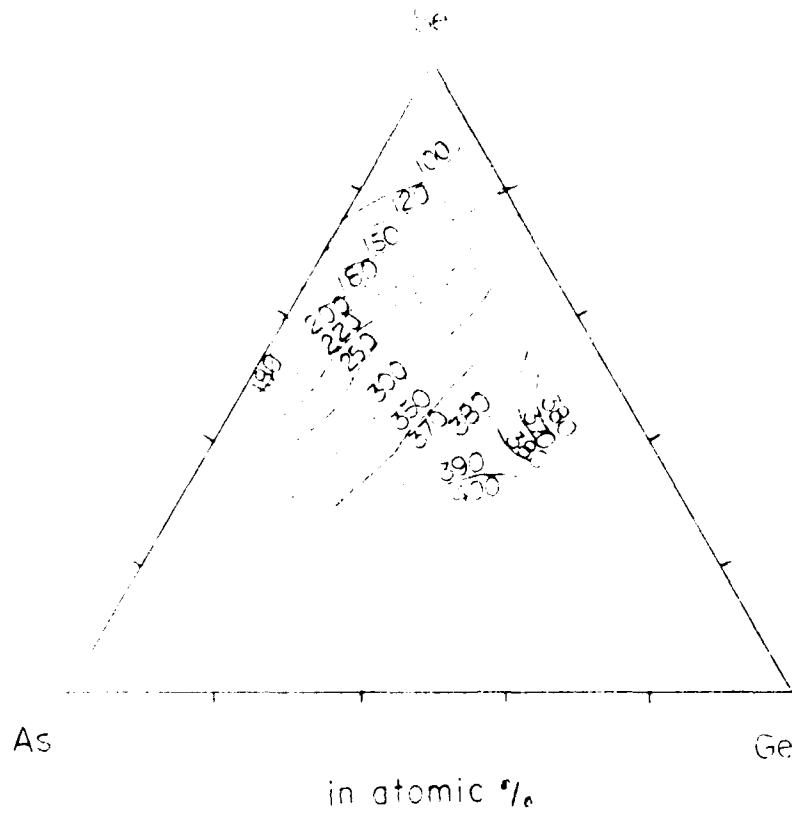


Figure 15. Glass Forming Region in Ge-As-Se System [Ref.53]

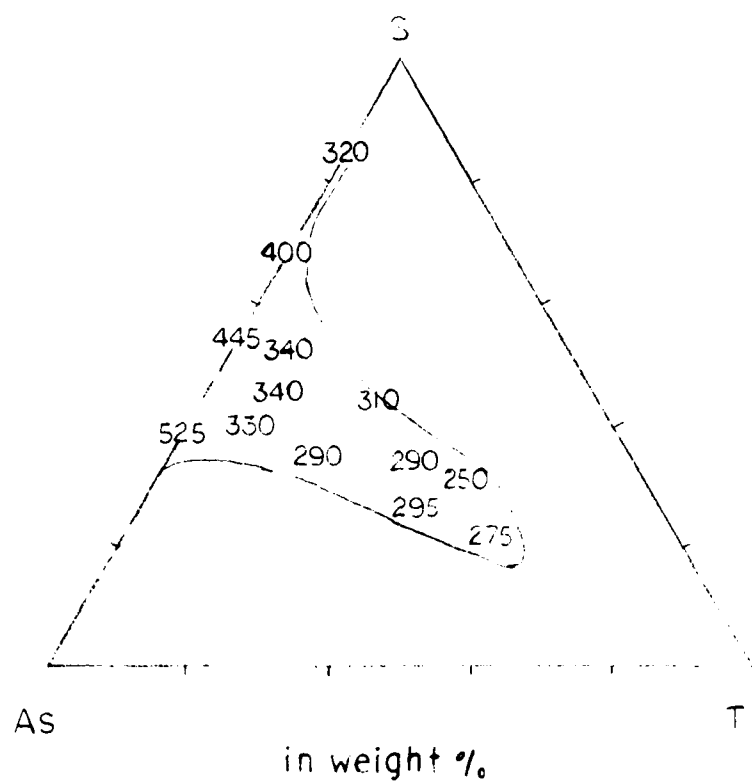


Figure 16(a) Glass Forming Region and Temperatures at which the Glasses Attain a Viscosity of 30 Poise in Tl-As-S System [Ref.11]

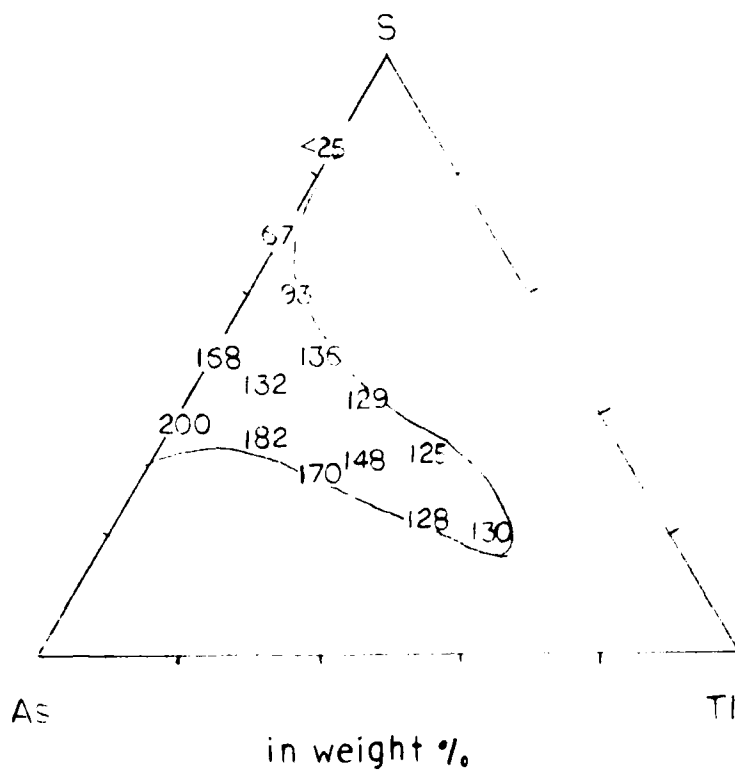


Figure 16(b) Glass Forming Region and Softening Temperatures of Tl-As-S System [Ref.11]

An addition of thallium to sulfide glasses decreases their viscosity drastically, whereas the additions of other large low charge elements such as Bi, Cd and Pb have little effect on viscosity of sulfide glasses. Flaschen et al [Ref.11] speculate that the melt structure is based on long sulfur chains with strongly bonded arsenic linkage and weakly bonded thallium linkage. The drastic decrease in viscosity is caused by the rupture of these weak thallium linkages upon heating. No evidence of devitrification has been observed in this system up to 125°C, while binary As-S glasses of high sulfur content ( 70 weight percent sulfur) precipitate sulfur at room temperature within a short period of time. This indicates that the thallium addition increases the glass stability of As-S glasses. The room temperature electrical conductivity of the glasses in this system is around  $10^{-12} \text{ohm}^{-1} \text{cm}^{-1}$ .

Tl-As-S glasses are useful as a low temperature hermetic sealing glass for electronic components because of their low softening temperature, low viscosity, good reactivity and wettability at molten state with many metals, low water solubility at room temperature, durability in dilute acids and oxidation resistance up to 110°C. However, they decompose slowly in alkali environment and are hygroscopic in boiling water.

The glass-forming region of Tl-As-Se [Ref.11 and 46], shown in Figure 17, is much larger than that in Tl-As-S system and it extends continuously to elemental selenium which itself forms a glass. The temperatures at which the glasses attain a viscosity

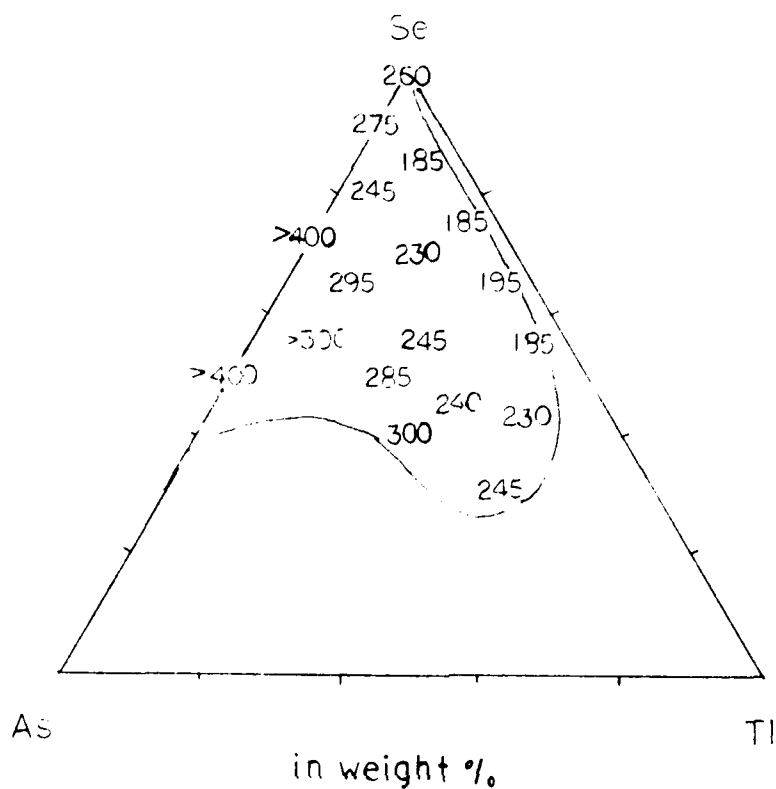


Figure 17. Glass Forming Region and Temperatures at which the Glasses Attain a Viscosity of 30 Poise in Tl-As-Se System [Ref.11]

of 30 poise are also shown in the figure. An addition of thallium to selenide glasses decreases their viscosity drastically, as seen in Figure 17. The chemical and physical properties of Tl-As-Se glasses are similar to those of Tl-As-S glasses except that the Tl-As-Se glasses in low selenium/high thallium region are semiconducting ( $\sim 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ ).

#### 9. As-Sb-S and As-Sb-Se

The glass-forming region in As-Sb-S system [Ref.46, 56 and 57] is shown in Figure 18. The glass-forming region near Sb-S tie line is bound by a liquid-liquid immiscibility region. On the  $\text{As}_2\text{S}_3$  -  $\text{Sb}_2\text{S}_3$  tie line, glasses form up to 70 mole percent  $\text{Sb}_2\text{S}_3$  content, under air quenching condition.

Kawamoto and Tsuchihashi [Ref.56] proposed that the  $\text{As}_2\text{S}_3$  -  $\text{Sb}_2\text{S}_3$  glasses form a microheterogeneous structure composed of  $\text{As}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_3$  regions, and the two regions are joined together by As-S-Sb linkages. When sulfur is added to the  $\text{As}_2\text{S}_3$ - $\text{Sb}_2\text{S}_3$  glasses [ref. 57], sulfur enters only into the  $\text{As}_2\text{S}_3$  region, and the  $\text{As}_2\text{S}_x$  ( $x > 3$ ) and  $\text{Sb}_2\text{S}_3$  regions become joined together by As-S-S-Sb linkages.

On the  $\text{As}_2\text{S}_3$  -  $\text{Sb}_2\text{S}_3$  tie line, refractive index varies from 2.58 for a low  $\text{Sb}_2\text{S}_3$  composition to 3.09 for a high  $\text{Sb}_2\text{S}_3$  composition. Their density increases with increasing  $\text{Sb}_2\text{S}_3$  content as expected.  $T_g$  is around  $190^\circ\text{C}$  throughout the compositional range.

Figure 19 shows the glass formation in As-Sb-Se system under air quenching or ice water conditions [Ref.58]. Homogenous

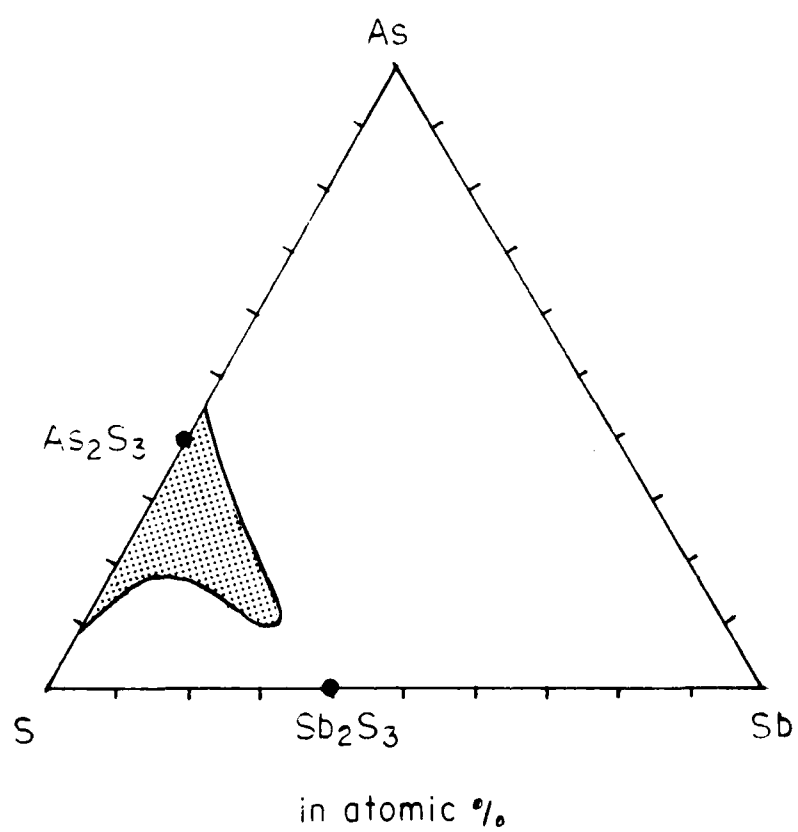


Figure 18. Glass Forming Region in As-Sb-S System [Ref.56]



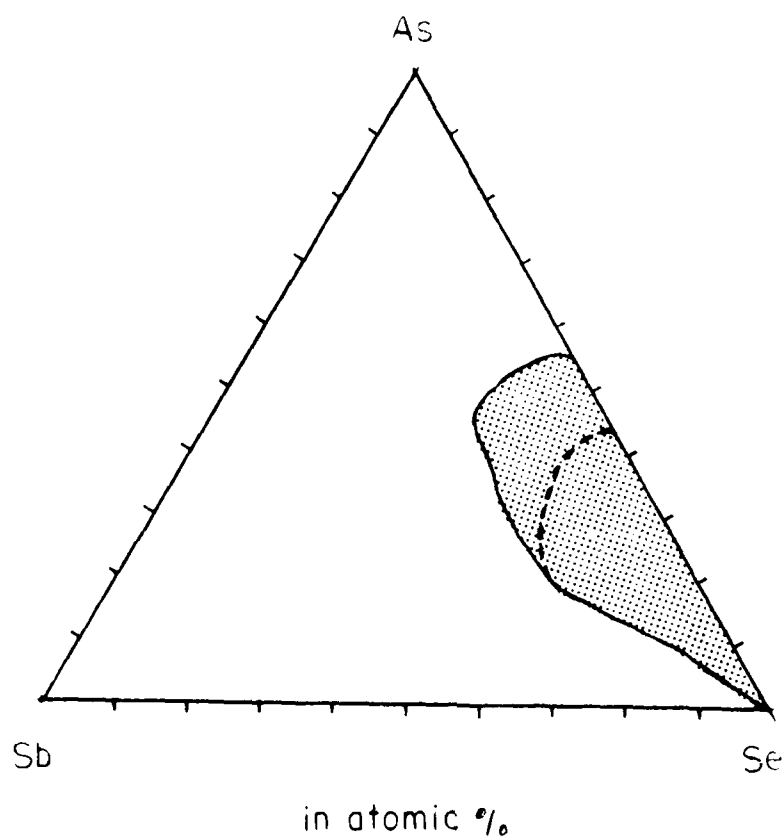


Figure 19. Glass Forming Region in As-Sb-Se System [Ref.58]

glasses have been found only in low selenium region enclosed within a broken line (-----) in Figure 19. On the  $\text{As}_2\text{Se}_3$  -  $\text{Sb}_2\text{Se}_3$  tie line, glasses form up to 40-50 mole percent  $\text{Sb}_2\text{Se}_3$  content [Ref.59, 60, 61 and 62]. The compositional effect on  $T_g$  has been found to be very small in  $\text{As}_2\text{Se}_3$  -  $\text{Sb}_2\text{Se}_3$  system, and  $T_g$  is around  $200^\circ\text{C}$  throughout the compositional range. An addition of selenium into the  $\text{As}_2\text{Se}_3$  -  $\text{Sb}_2\text{Se}_3$  system decrease their  $T_g$  [Ref.58].

On the  $\text{As}_2\text{Se}_3$  -  $\text{Sb}_2\text{Se}_3$  tie line, an addition of  $\text{Sb}_2\text{Se}_3$  to  $\text{As}_2\text{Se}_3$  decreases the viscosity of the melt and quickens the crystallization kinetics. The crystallized phases have a higher antimony content as compared to the surrounding amorphous matrix. The compositions with low  $\text{Sb}_2\text{Se}_3$  content crystallizes in monoclinic crystal structure, whereas the compositions rich in  $\text{Sb}_2\text{Se}_3$  crystallizes in orthorhombic structure. The crystallization rate has been found to be composition dependent in monoclinic region, and composition independent in orthorhombic region [Ref.60].

#### 10. As-Halogen-(S,Se or Te)

The glass-forming region of As-I-S system under air quenching condition is shown in Figure 20(a) and Figure 20(b) [Ref.63]. The glass-forming region is bound by a liquid-liquid immiscibility region at high sulfur concentrations, and by a crystal-forming region at low sulfur concentration. The temperatures at 30 poise viscosity are shown in Figure 20(a). Iodine atoms act as chain terminators and reduce the viscosity of

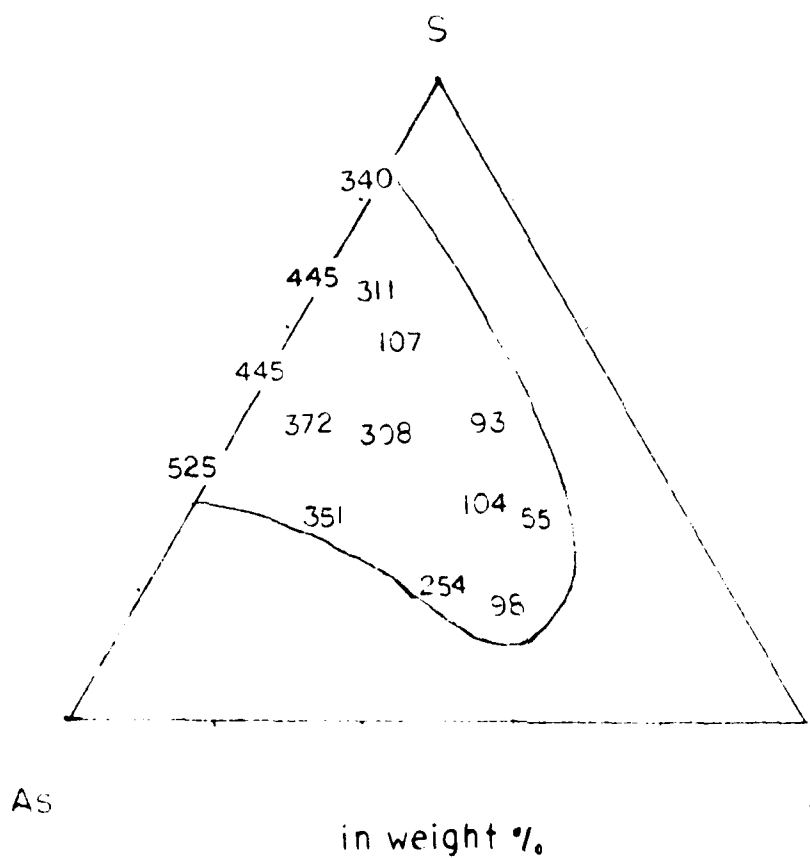


Figure. 20(a) Glass Forming Region and Temperatures at which the Glasses Attain a Viscosity of 30 Poise in As-I-S System [Ref.63]

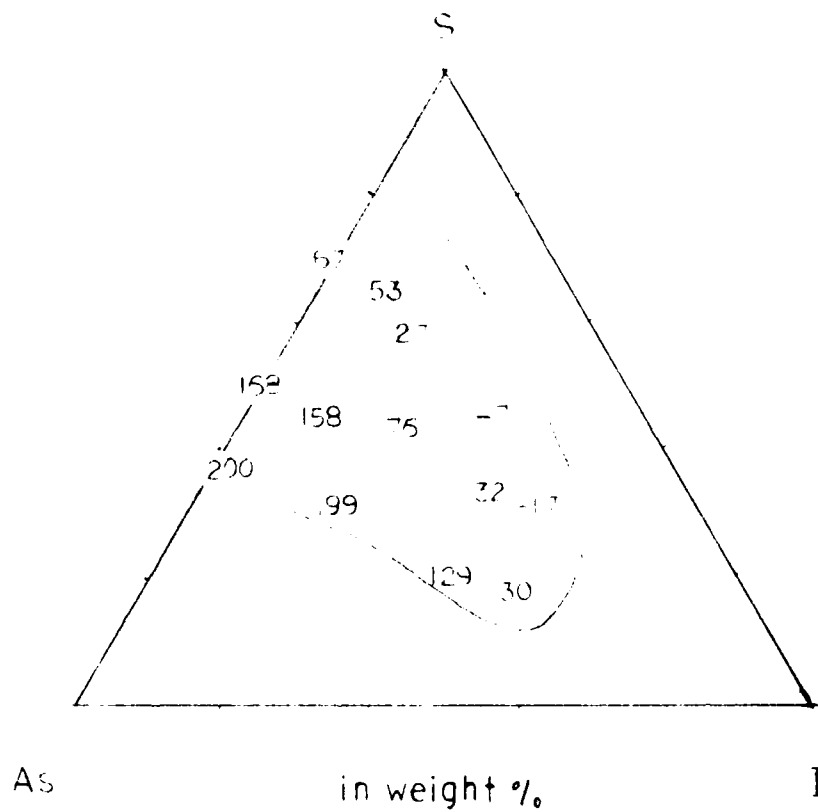


Figure. 20(b) Glass Forming Region and Softening Temperatures of As-I-S System [Ref.63]

As-S glasses drastically. The softening points are shown in Figure 20(b). As-I-S glasses are reported to have an excellent resistance to moisture and to acids, including hydrogen fluoride [Ref.64]. The room temperature electrical conductivity is around  $10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

Figure 21 shows the glass-forming region of As-I-Se system under air quenching condition [Ref.65]. The viscosity of As-I-Se glasses decreases with increasing iodine concentration. The glasses are chemically stable and sodium hydroxide is one of the few reagents found to chemically attack those glasses. The room temperature electrical conductivity decreases with increasing iodine concentration, and varies from  $10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$  to  $10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

The glass-forming region and the constant conductivity contours in As-I-Te is shown on Figure 22 [Ref.66, 67 and 68]. The glasses in As-I-Te system range in color from black for high iodine concentrations to silvery black for low iodine concentrations. The softening temperatures of the compositions range from  $100^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ . The room temperature conductivity range from  $10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  for high iodine concentrations to  $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  for low iodine concentrations as shown in Figure 22. These glasses exhibit bistable electrical switching and memory effect.

Figure 23 shows the glass-forming region in As-Br-S system [Ref.67]. Most of the solid glasses in As-S-Br system are stable against devitrification at room temperature. However, some compositions near high sulfur boundary of the glass-forming

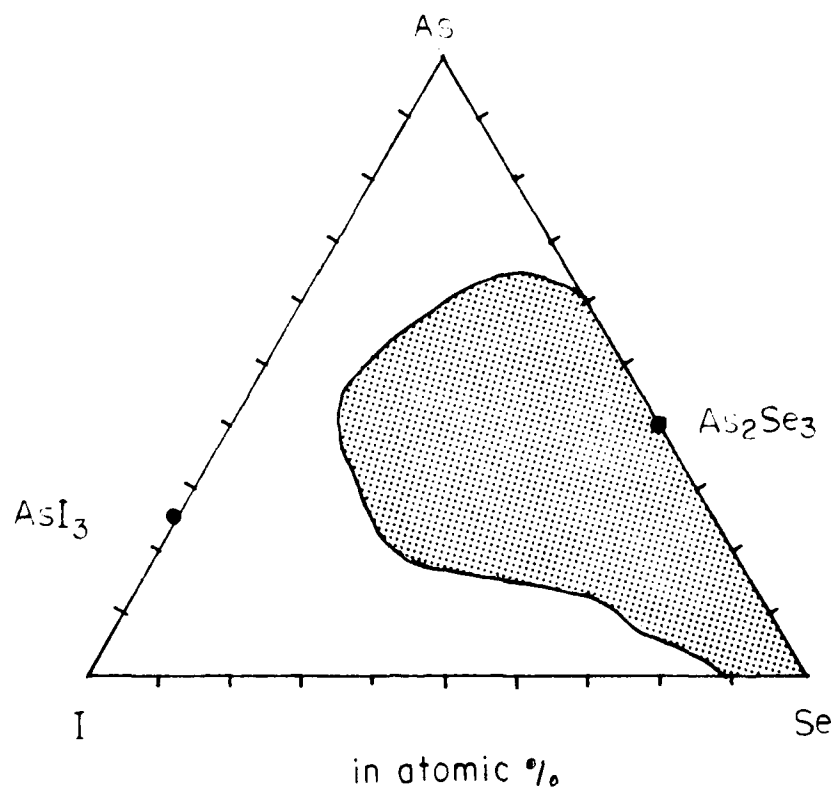


Figure 21. Glass Forming Region in As-I-Se System [Ref.65]

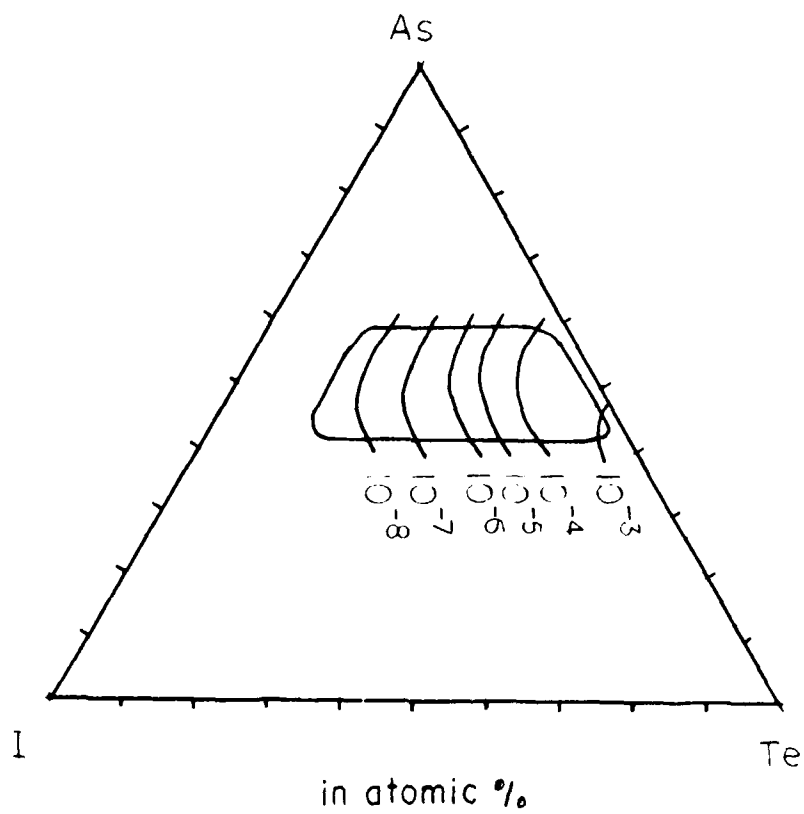


Figure 22. Glass Forming Region and Constant Electrical Conductivity Contours in As-I-Te [Ref.66]

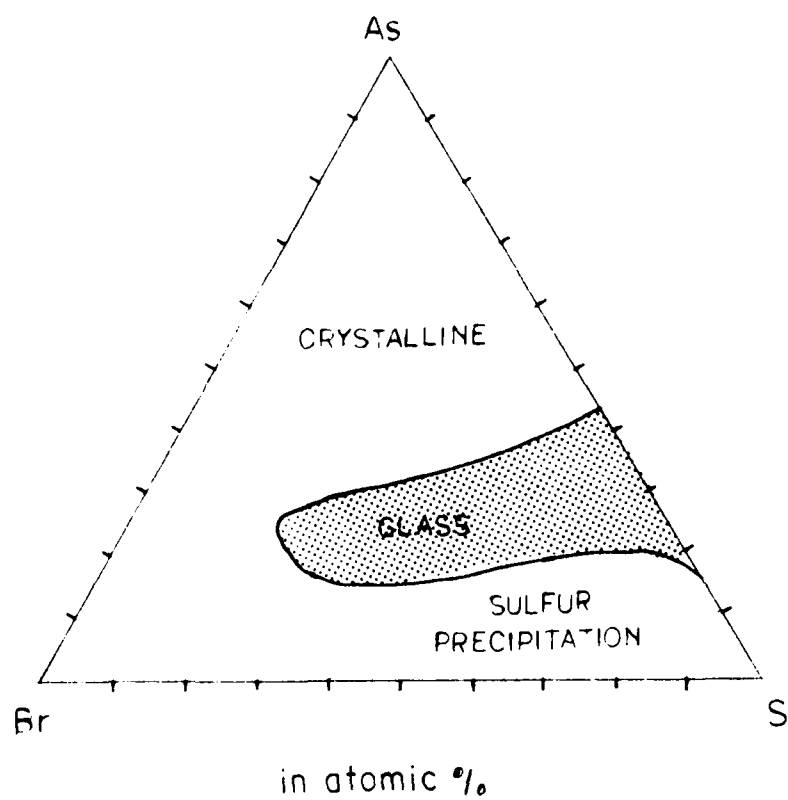


Figure 23. Glass Forming Region in As-Br-S System [Ref.67]



region are reported to show sulfur precipitation . The glasses range in color from a deep ruby red of  $\text{As}_2\text{S}_3$  to a pale transparent yellow at high bromine concentrations. The color of all the compositions darken with increasing temperature. An addition of bromine causes viscosity to decrease drastically, and  $\text{As}_{19}\text{Br}_{47}\text{S}_{34}$  is as fluid as water at room temperature with a softening temperature of  $-60^\circ\text{C}$ . The room temperature electrical conductivity is reported to be lower than  $3 \times 10^{-15} \text{ ohm}^{-1} \text{ cm}^{-1}$  for all compositions. The refractive index decreased with increasing bromine content.

#### 11. As-(others)-(S or Se)

Figures 24(a)-(d) summarize the glass-forming regions in the systems As-M-Se, where M=Au, Ag, Cu, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb and Ge. The extent of glass-forming regions in As-M-S systems are compared with that in As-M-Se systems in Figures 25(a) and Figure 25(b) [Ref.69 and 70].

A small amount of tin (up to 5 atomic percent) can be incorporated into As-Se glasses to form As-Sn-Se glasses [Ref.71 and 72]. However, tin rich phase has been found to segregate, leading to a microheterogeneous glass structure.

In  $\text{As}_2\text{S}_3$ -PbS system, glasses are reported to form up to more than 50 atomic percent PbS content [Ref.73, 74 and 75]. These glasses phase separate into two glassy phases which crystallize at different temperatures. The softening temperature is around  $200^\circ\text{C}$ .

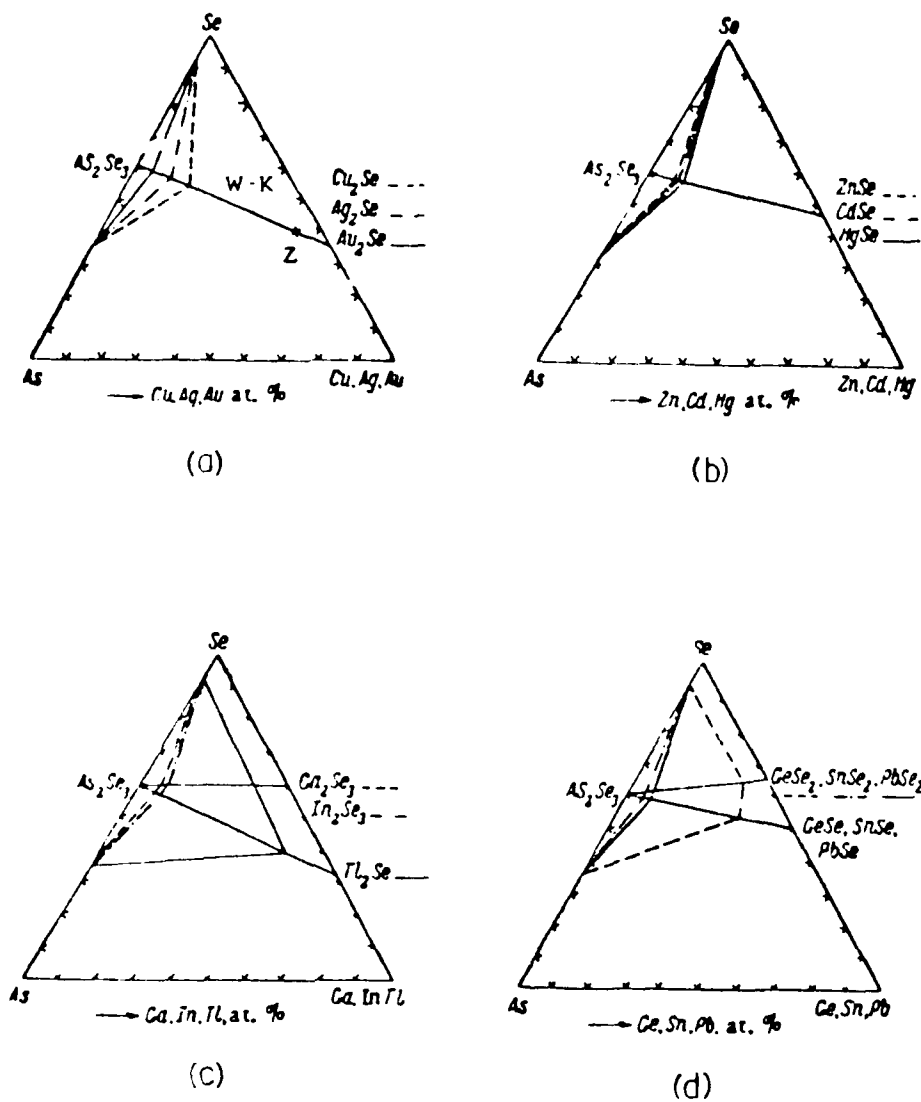


Figure 24. Glass Forming Region in As-M-Se System [Ref.69]  
 (a) M = Au, Ag and Cu ; (b) M = Zn, Cd and Hg  
 (c) M = Ga, In and Tl ; (d) M = Sn, Pb and Ge

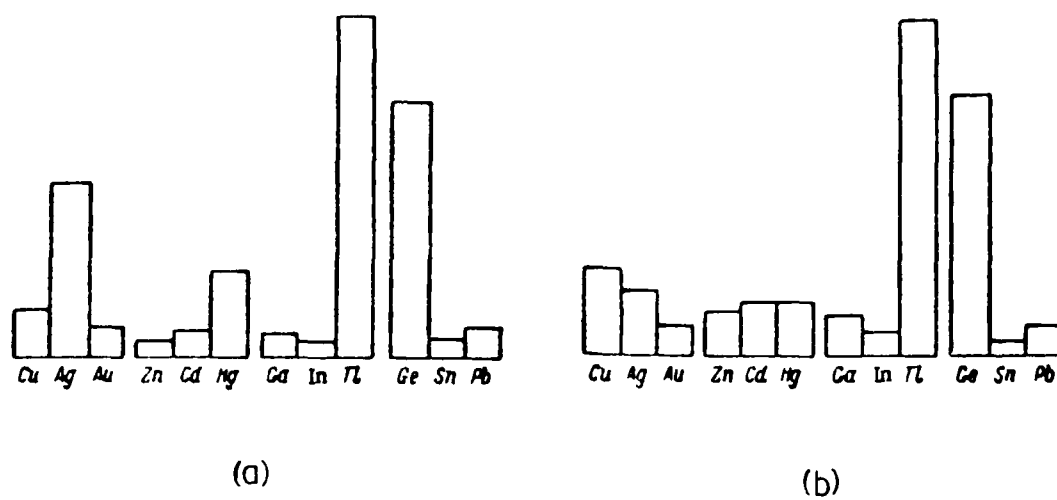


Figure 25. Extent of Glass Forming Region in (a) As-M-S System and (b) As-M-Se System, where M = Cu, Ag, Au, Zn, Cd, Hg, Ca, In, Tl, Ge, Sn and Pb [Ref.69]

## 12. Group IV-Sb-(S or Se)

The glass-forming regions in the Si-Sb-S system and the Si-Sb-Se system are shown in Figures 26 and 27, respectively. The region enclosed with a dotted line in Figure 26 represents a region in which a homogeneous glass forms over an immiscible antimony rich alloy. These glasses have been found to be chemically unstable and reactive to the atmospheric water with evolution of  $H_2S$  gas. Some of the glasses in these systems have a high softening temperature around  $450^{\circ}C$  [Ref.30].

Figure 28 shows the glass-forming region in Ge-Sb-S system under cold water quenching condition [Ref.76]. The glass formation and  $T_g$  in Ge-Sb-Se [Ref.39 and 40] are shown in Figure 29.  $T_g$  varies from  $60^{\circ}C$  for selenium to  $350^{\circ}C$  for low selenium glass in Ge-Sb-Se system. Along with TI-20 glass ( $Ge_{33}As_{12}Se_{55}$ ), TI-1173 glass ( $Ge_{28}Sb_{12}Se_{60}$ ) is a commercially available infrared optical glass. Physical and optical properties of TI-1173 glass is similar to that of TI-20 glass. TI-1173 glass has lower optical absorption as compared to TI-20 glass at  $10.6\mu m$ , and is better suited for use in  $CO_2$  laser optical systems [Ref.40, 55 and 77].

## 13. Ge-Bi-(S or Se)

The glass-forming region in Ge-Bi-S system under cold water quenching condition is relatively small as shown in Figure 30 [Ref.78]. The samples with more than 5 atomic percent bismuth concentration crystallized relatively easily above  $T_g$ .  $T_g$  of the glasses varies from around  $280^{\circ}C$  for low bismuth

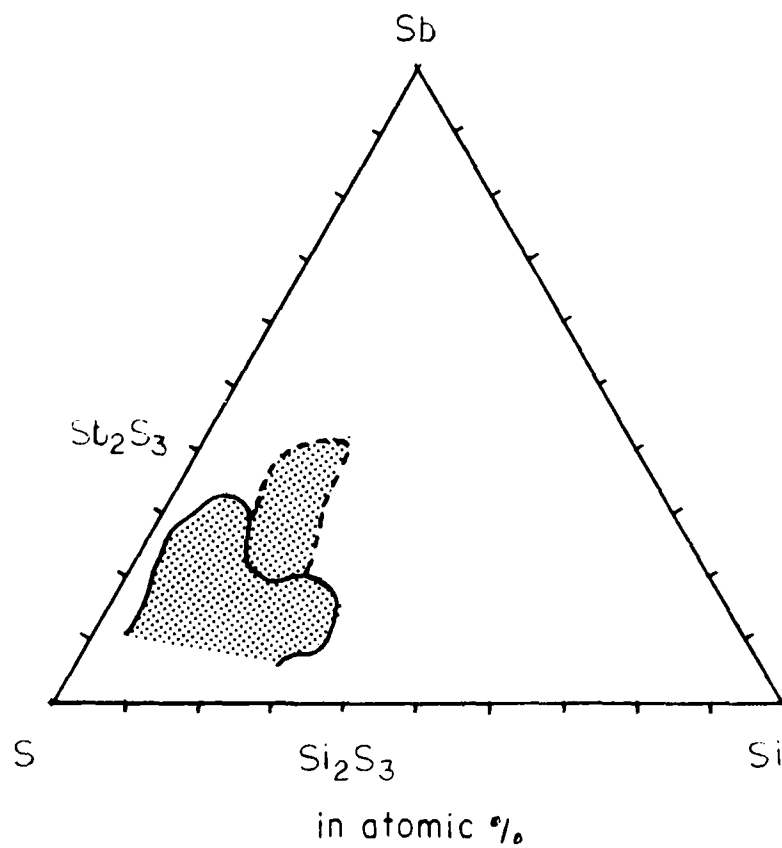


Figure 26. Glass Forming Region in Si-Sb-S System [Ref.30]

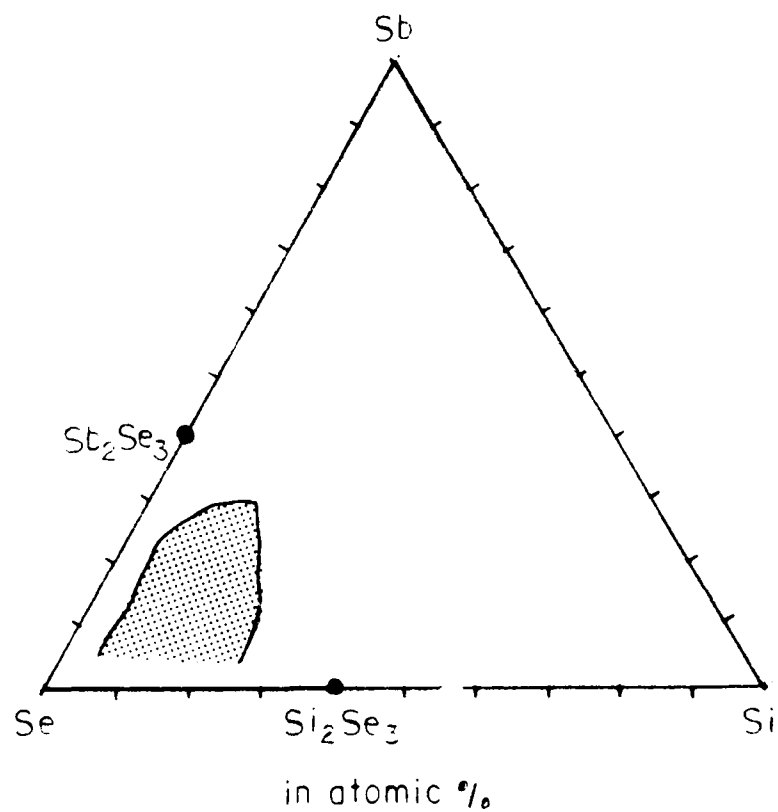


Figure 27. Glass Forming Region in Si-Sb-Se System [Ref.30]

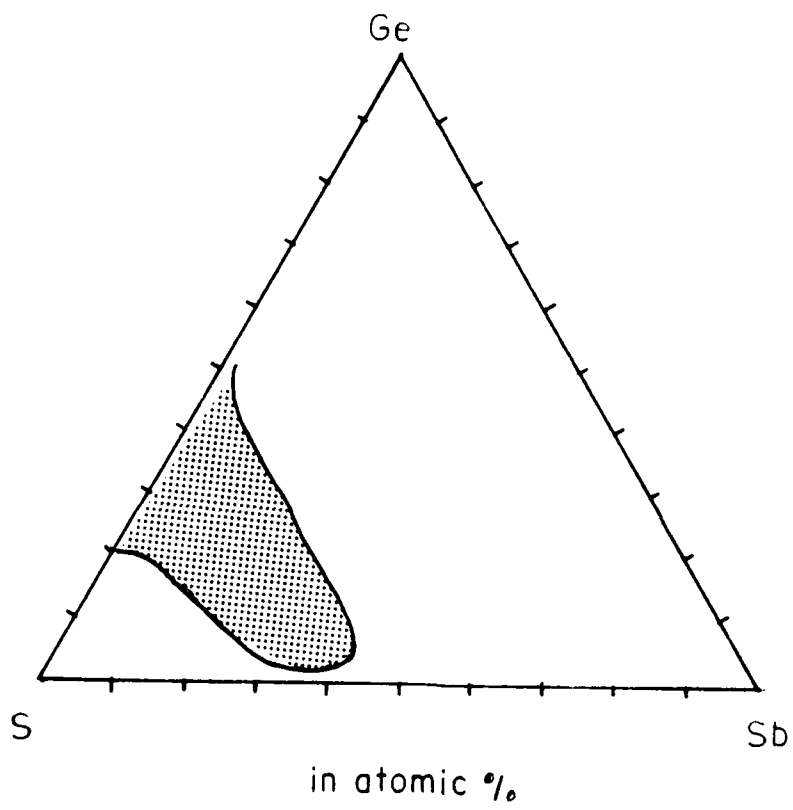


Figure 28. Glass Forming Region in Ge-Sb-S System [Ref.76]

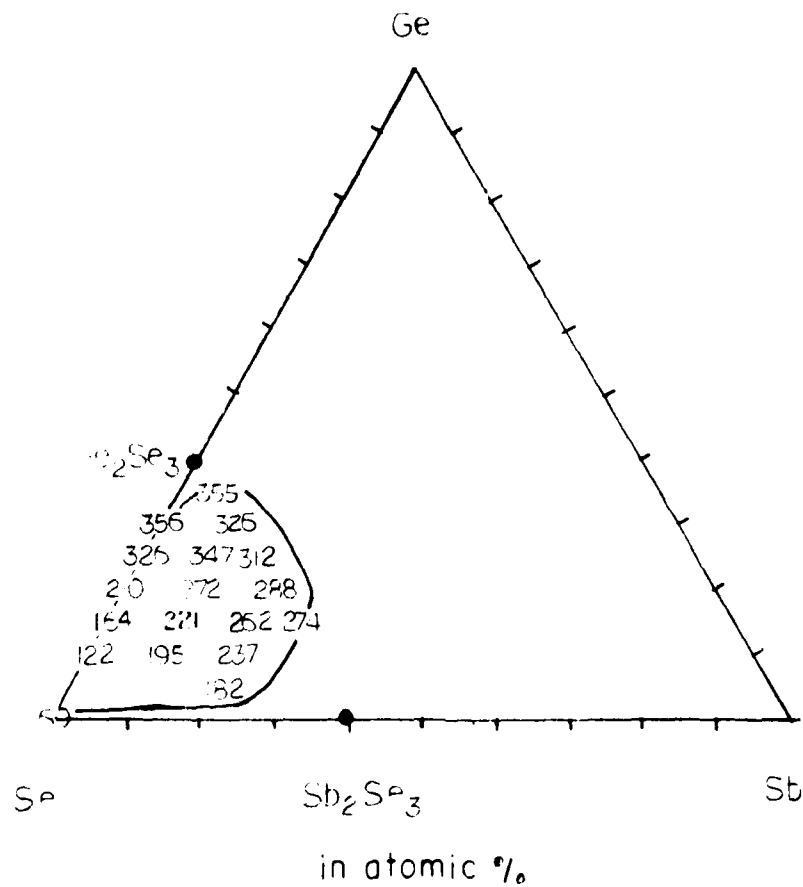


Figure 29. Glass Forming Region and T<sub>g</sub> in Ge-Sb-Se System.  
[Ref. 40]



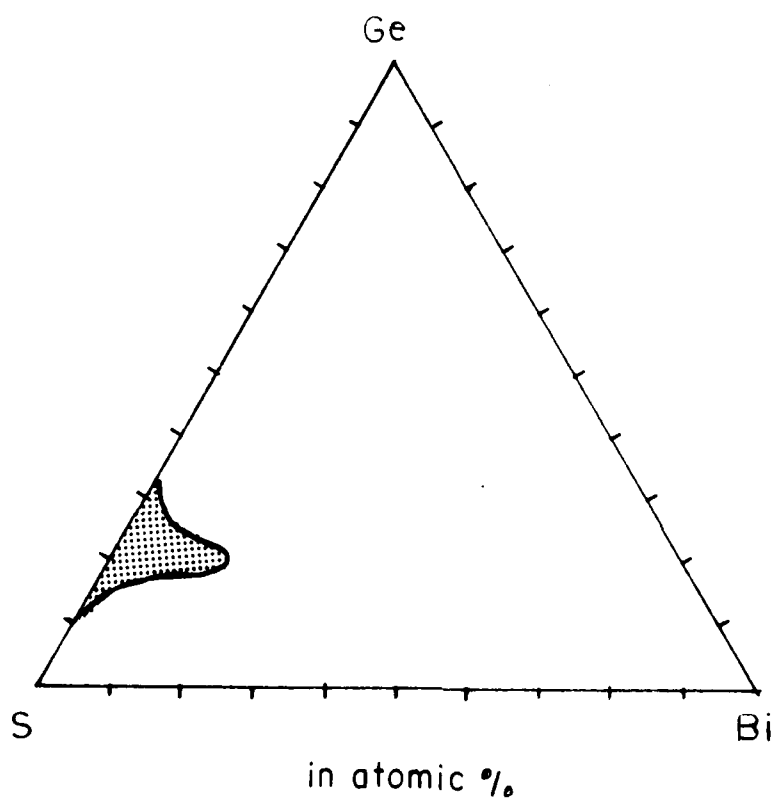


Figure 30. Glass Forming Region in Ge-Bi-S System [Ref.78]

concentration to 300°C for high bismuth concentration. The room temperature electrical conductivity varies from  $10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$  for  $\text{Ge}_{20}\text{Bi}_5\text{S}_{75}$  to  $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$  for  $\text{Ge}_{20}\text{Bi}_{15}\text{S}_{65}$ .

The glass-forming region in Ge-Bi-Se system is shown in Figure 31. The broken line indicates the glass formation with air quenching condition [Ref.79], and the solid line indicates the liquid nitron quenching condition [Ref.41]. The physical properties of Ge-Bi-Se system are similar to that of Ge-Bi-S system.

#### 14. Ge-Sn-Se

Relatively large glass-forming region for Ge-Sn-Se shown in Figure 32 [Ref.42] has been obtained under vapor quenching condition. Under air quenching condition, only small amount (up to 10 atomic percent) of tin can replace germanium. The softening temperature and hardness decrease with increasing tin content. [Ref.80]

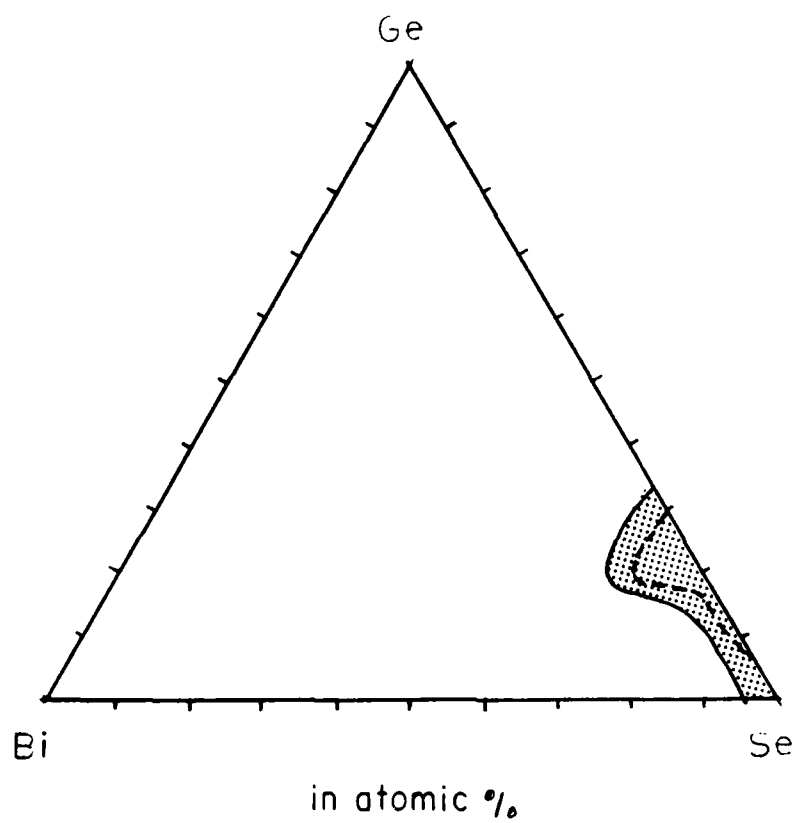


Figure 31. Glass Forming Region in Ge-Bi-Se System  
[Ref.41 and 79]

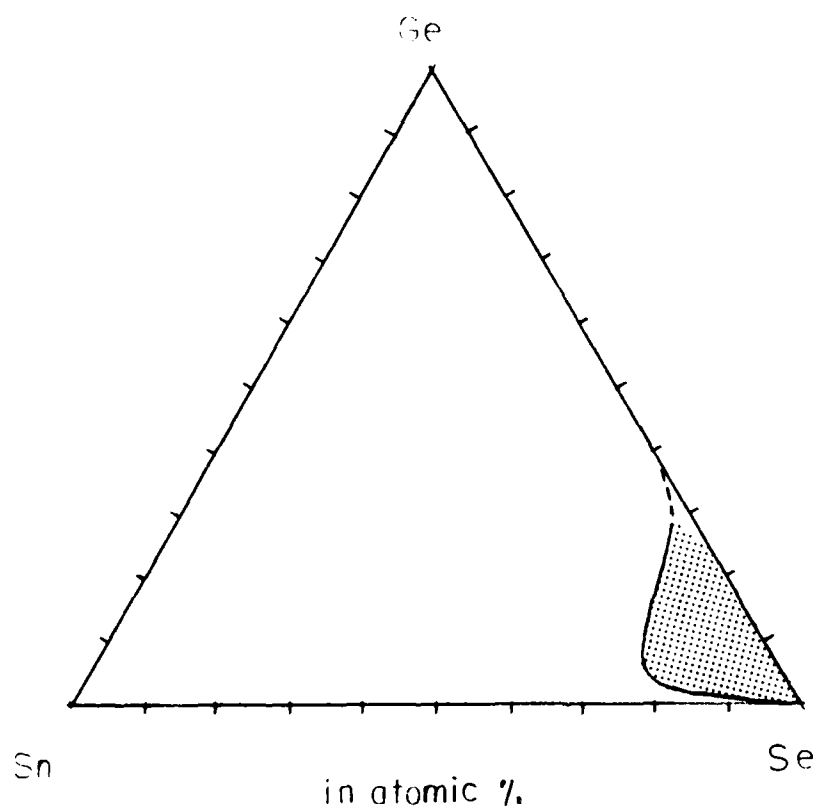


Figure 32. Glass Forming Region in Ge-Sn-Se System [Ref.42]

#### IV. Glasses with Four or More Components

##### 1. As-Si-Se-Te-Ag and Ge-As-Se-Te

As-Si-Te glass system has been explored as an infrared optical component operative from  $3\mu\text{m}$  to  $14\mu\text{m}$ , since this glass system has the highest softening temperature among all selenide and telluride glasses. A replacement of tellurium with selenium in the As-Si-Te glasses makes the glasses more refractory while maintaining sufficient optical transmission in the long wavelength region. However, selenium can not be incorporated into silicon containing glasses as a stable component, and it volatilizes as either  $\text{H}_2\text{Se}$  gas or  $\text{SeO}_2$  gas. Anthonis, et al (Ref.50) have found that an addition of silver as a modifier permits the incorporation of selenium into the As-Si-Te glasses. The softening temperatures of As-Si-Se-Te-Ag are reported to be up to  $150^\circ\text{C}$  higher than that of As-Si-Te glasses. This is due to a second phase with higher softening temperature. The phase separation manifests at higher Ag-Se concentration, which is detrimental to the optical transmission. Though Anthonis, et al also investigated other modifiers such as Sb, P, Ge, Al, Bi, Pb and Zn, they were less successful in elevating the softening temperature and in most cases they induced devitrification.

Ge-As-Se-Te glasses were also developed for use in infrared optical applications [Ref.81]

## 2. As-Si-Ge-Te-(X) and Tl-As-Se-Te

Thin films of As-Si-Ge-Te glasses with or without a fifth component ( $X = P, I$  or  $Mn$ ) have been investigated by many researchers [Ref.82-91] because of their non-linear electrical current-voltage characteristics. The most well studied composition in this glass system is  $As_{35}Si_{18}Ge_7Te_{40}$ , which was originally reported by Ovshinski in 1968 [Ref.82].

A memory switching; a permanent or semi-permanent change in electrical conductivity from a resistive state to a conductive state, and a threshold switching; a very fast reversible change in electrical conductivity, in glassy chalcogenide films have been extensively investigated for use as a new type of switching diodes. These glasses may be used as switching diodes or memory cells, because they exhibit a non-linear I-V characteristics upon application of high electric field. A switching transition develops when a critical electric field (materials characteristic internal field of  $\sim 5 \times 10^5$  V/cm) is reached somewhere in the specimen, usually near an electrode. The mechanism of these switching phenomena may be both electronic (field induced carrier generation) and thermal (field induced phonon generation). It is, by now, well accepted that the switching process progresses by the formation of filamentary, low resistance path, in which the micro-crystallization takes place with the speed of sound (4000 m/sec). The diameter of the filaments has been observed to be  $2 \sim 25 \mu m$ . A phase separation of submicron particle size seems to enhance the switching characteristics.

The glasses in  $(\text{Tl}_2\text{Se})_x(\text{As}_2\text{Te}_3)_{1-x}$  system in a thin film form have been investigated as a chalcogenide optical switch material [Ref.92-94]. These glasses are amorphous semiconductors with temperature dependent optical absorption, in which the optical transmission decreases as a result of runaway carrier absorption upon laser heating. They are stable glasses, which can be cycled through their glass transition temperature range. For a composition  $\text{Tl}_2\text{Se As}_2\text{Te}_3$ , the glass transition is at  $80^\circ\text{C}$ , and the order disorder transition is at  $202^\circ\text{C}$ .

### C. SUMMARY

Glass-forming regions and relevant physical, chemical and structural properties of chalcogenide glass compositional systems have been compiled through extensive literature search. In general, the glass-forming ability decreases as the atomic number of constituent element increases and subsequently, their bonding type changes from dominantly covalent to more metallic. For this reason, the glasses containing tellurium are noted for higher electrical conductivity and poorer glass-forming ability, as compared to sulfides and selenides. In addition, telluride glasses and multicomponent glasses containing tellurium have more tendency to phase separate, leading to heterogeneous micro structures which are not suitable in the optical applications. Formation of homogeneous glasses with varying compositions which are stable against crystallization and phase separation should be possible on quasi binary tie lines between two excellent glass formers, such as  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$  and  $\text{GeS}_2$ . The microstructural data in chalcogenide glass systems are very scarce. Little data exists on long term stability of the chalcogenide glasses, particularly in thin film form, at elevated temperatures which are needed for filter fabrication processes.



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